THE EMISSIONS OF NITROUS OXIDE FROM AGRICULTURAL FIELDS IN NEW YORK STATE: EFFECT OF FERTILIZATION AND ANALYSIS OF TEMPORAL AND SPATIAL VARIABILITY

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THE EMISSIONS OF NITROUS OXIDE FROM AGRICULTURAL FIELDS IN NEW YORK STATE: EFFECT OF FERTILIZATION AND ANALYSIS OF TEMPORAL AND SPATIAL VARIABILITY

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The atmospheric nitrous oxide (N_2O) is of special interest, due to its persistent effect as a potent greenhouse gas and stratospheric ozone destructor. Animal manure fertilization is one of the key factors contributing to N_2O formation. In the Northeastern US, dairy industry is the largest agricultural activity, and the manure cropland fertilization is a common practice.

Continuous monitoring of N_2O emissions from croplands in New York State was conducted by eddy covariance method from 2006 to 2009. The research was aimed at quantification of N_2O emissions from manure-fertilized corn (*Zea mays*) and alfalfa (*Medicago sativa*) fields, estimating strength and spatial variability of soil N_2O sources by conducting simultaneous static chamber campaign, and analysis of temporal distribution of N_2O fluxes as affected by seasonality of climate variations and manure practices.

The analysis of cumulative N_2O emissions and source contributions into the integrated flux showed that manure nitrogen (N) was the most important factor controlling the extent of N_2O formation: areas which received more manure N were stronger N_2O emitters. Whereas N availability determined a magnitude of N_2O emissions, the environmental changes altering soil moisture and temperature status were major N_2O

event triggers. The temporal flux distribution demonstrated episodic event-induced nature of N_2O peak fluxes, which were primarily driven by strong rainfall and warm temperatures in growing season and soil thaw in winter and early spring. The greatest N_2O emissions were observed when flux-triggering weather events coincided with or followed manure application. The most intense single N_2O peak event was produced from combination of summer manure spreading and strong rainfall; however spring thaw-induced N_2O fluxes showed more consistent seasonal year-to-year trend.

The daily average fluxes measured by the EC and chamber techniques were in good agreement. The spatial variability of chamber measurements was mainly caused by high heterogeneity of soil N_2O formation, which resulted both in net N_2O production and consumption. The EC integrated flux was strongly dependent on wind direction and contributing footprint. The combination of the two different scale methods may help in reducing temporal and spatial variability of N_2O estimates and improving N_2O emission data quality.

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BIOGRAPHICAL SKETCH

Marina Molodovskaya was born in Tashkent, Uzbekistan, in 1970. She graduated from the high school and enrolled to study Chemistry at Tashkent State University in 1987. Marina completed five-year academic program and graduated with Honor in Chemistry in 1992. After graduation, she started working as environmental scientist at the Department of Environmental Research and Forecasts of Central Asian Research Hydrometeorological Institute in Tashkent. In 1999, Marina completed three-month post-graduate course on Exploration, Exploitation and Management of Groundwater Resources in Hebrew University of Jerusalem, Israel. In 2002-2003, she worked with the international NGO "Doctors without Borders" Aral Sea Area Program in Central Asia, where she had a unique opportunity to participate in the research of environmental impact on public health in the region of ecological disaster. Marina was awarded Edmund S. Muskie/FSA Graduate Program Fellowship, which allowed her joining Soil and Water Group at the Department of Biological and Environmental Engineering, Cornell University, in August 2003. After obtaining Master of Science degree in Agricultural and Biological Engineering in August 2005, she continued working on her Ph.D. project in the same group.

To my family

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CHAPTER 1

INTRODUCTION

The accumulation of nitrous oxide (N_2O) alters the chemical composition of the atmosphere, adds to the global greenhouse gas effect (8 percent of global total) and affects stratospheric ozone chemistry. In terms of greenhouse gas potential, each kg of N_2O is equivalent to nearly 300 kg of carbon dioxide (CO_2) due to extended atmospheric residence times (IPCC, 2001).

The atmospheric concentration of N_2O has risen by 17 percent over the past 250 years with acceleration in the rate of increase during the last 50-60 years. Future scenarios predict an almost 1.5-fold increase in N_2O emissions between 1990 and 2020 (EPA, 2006).The intense buildup of N_2O is largely caused by global agriculture which strongly alters the reactive nitrogen (N) cycle. Emissions of nitrous oxide from agricultural soils constitute 38 percent of all non-CO_2 greenhouse gases from agriculture and are projected to increase by 47 percent from 1990 to 2020 (EPA, 2006). Nitrogen fertilization is believed to be one of the major contributors to agricultural soil N_2O formation.

The Northeastern US, and New York State in particular, is characterized by a high concentration of dairy farms, and manure fertilization of croplands is a common practice. Dairy farming significantly contributes to regional N-cycling by importing N in feed and fertilizer and accelerating N-fixation rates through cultivated leguminous crops (e.g., alfalfa and clover). There is little known about the magnitude of N_2O release in the region, although indirect estimates of the regional N budget indicate high potential for N losses with gaseous emissions (Boyer et al., 2002). Understanding of N_2O formation in manure fertilized soils is therefore essential for developing nutrient management strategies to reduce adverse environmental impacts.

High-frequency monitoring of N_2O emissions from manure-fertilized corn (*Zea mays*) and alfalfa (*Medicago sativa*) fields in New York State was carried out using micrometeorological eddy covariance (EC) method from 2006 to 2009. This study was the first effort to investigate year-round N_2O emissions from dairy farming in the Northeast US on a long-term continuous basis. The main objectives of this research were: (a) to quantify N_2O emissions from alfalfa and corn fields as affected by manure N fertilization; (b) to analyze strength and spatial variability of soil N_2O sources within non-uniform landscapes; (c) to estimate the temporal distribution of N_2O fluxes as affected by seasonality of climate variations and manure practices.

These research objectives are addressed in Chapters 2 to 4 of this dissertation. Chapter 2 discusses the effect that manure N inputs had on the magnitude of monthly N_2O fluxes from alfalfa and corn fields during growing season of 2006 and years of 2007-2008. It also gives an estimate of fertilizer-induced N_2O emission factors defined as the percentage of N input from fertilization that is converted to N_2O and compares them with default IPCC values. Chapter 3 focuses on the spatial variability of soil N_2O formation and contributions of N_2O sources and sinks to the integrated micrometeorological flux. A short-term campaign using an array of static chambers was conducted concurrently with the eddy covariance system to compare and cross-validate N_2O measurements at differing footprint scales. Chapter 4 emphasizes the importance of high N_2O peaks in the annual cumulative flux, gives an insight into seasonal patterns of emissions distribution, and analyzes the complex nature of climatic and anthropogenic parameters triggering the high magnitude N_2O events.

Chapters 2 to 4 thus represent a coherent research line. However, they have been written as standalone papers to facilitate publication in peer-reviewed journals, resulting in some necessary redundancy in the descriptions of instrumentation and experimental sites. Each Chapter contains complete “Introduction”, “Materials and Methods”, “Results” and “Discussion” sections and discrete lists of literature references. Chapter 5 provides a summary of the results and conclusions.

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CHAPTER 2

CONTINUOUS EDDY COVARIANCE MONITORING OF NITROUS OXIDE EMISSIONS FROM MANURE-FERTILIZED ALFALFA AND CORN CROPLAND IN NEW YORK STATE

2.1 Introduction

The detrimental loss of nitrogen (N) from soil fertilization is an important environmental problem of modern agriculture. Among the threats that elevated N poses to the environment, the increase in net nitrous oxide (N_2O) production is of special interest due to its persistent atmospheric effect as a potent greenhouse gas and stratospheric ozone destructor. As one of the key factors for agricultural N_2O formation (Mosier et al., 1998; Kroeze et al., 1999), animal manure fertilization can result in up to 4% of manure N released as N_2O gas (Rochette et al., 2004; van Groenigen et al., 2004; Webb et al., 2004; Liebig et al., 2005). There is serious concern that as agro-biofuel crop production intensifies any net gain from reduced fossil fuel carbon dioxide (CO_2) emissions could be offset by the increase in atmospheric N_2O from additional soil fertilization (Crutzen et al, 2007).

During the last decade, numerous databases on N_2O emissions from fertilized lands have been created and analyzed (Bouwman et al., 2001; Helgason et al., 2005; Stehfest et al., 2006; Flechard et al., 2007), and current knowledge about the factors effecting N_2O formation in agricultural and natural soils is constantly improving. Nevertheless, the majority of studies represent episodic campaign measurements rather than continuous observations, and N_2O data from regular long-term monitoring of fertilized fields are still lacking.

In the Northeastern US, little is yet known about the magnitude of agricultural nitrous oxide release. Boyer et al. (2002) found that riverine exports represent only a fraction of net N imports for 16 watersheds in the Northeast, implying large gaseous emissions. Whereas the majority of manure N losses occur as ammonia volatilization, there is a potential for significant denitrification and N_2O formation, since many soils in the Northeast are underlain by dense glacial tills that result in seasonal shallow perched water tables and soil saturation. The dairy industry is the largest agricultural activity in the Northeast, with the significant proportion of purchased feed as a potential source of excess nutrients, and the manure land fertilization as a common practice. By a recent survey of New York State dairy farms, up to 78% of the N imported in purchased feed can remain in the fields as residue or returned as manure, significantly contributing to the regional N budget and potential N_2O emissions (NNYADP 2005). On farms with manure storage facilities, manure is usually spread and incorporated either before the beginning of growing season or after the crop harvest, but on those without sufficient storage the manure must be spread throughout the year on whatever land is available at the time.

The timing of manure application can strongly influence N_2O emissions, as many studies report that most N_2O is evolved during the spring thaw and growing season subsequent to the application of N fertilizer (Goodroad et al., 1984; Cates and Keeney, 1987; Wagner-Riddle et al., 1998; Wagner-Riddle et al., 2007; Singurindy et al., 2009). Tillage practices can also affect emissions. Whereas most New York fields are conventionally tilled (Hahn, 2006), conservation tillage practices such as chisel-plowing and no-till are also used (Fick and Cox, 1995). Although observed effects of tillage on N_2O emissions vary (Helgason et al., 2005), some studies showed greater N_2O fluxes from conventional tillage than from no-till (Wagner-Riddle et al., 2007;

Sey et al., 2008). Variations in emissions are possible even between two adjacent field portions tilled at different times relative to manure spreading events (Singurindy et al., 2009).

The two primary feed crops for dairy farming in New York State are corn (*Zea mays* L.) and alfalfa (*Medicago sativa* L.), typically grown in rotation. It is at present unclear how different cropping systems combined with manure practices affect total N_2O emissions, although some studies have focused on particular manure-fertilized crops (Cates and Keeney, 1987; Wagner-Riddle et al., 1996; Gamba et al., 1998; Yan et al., 2001; Sey et al., 2008). There are some implications that leguminous N-fixing crops (e.g., alfalfa) have greater potential to generate additional N_2O during decomposition of excess N in plant residues and/or release by *Rhizobium* during N-biofixation (Helgason et al., 2005). However, due to the lack of continuous data this hypothesis has been neither confirmed nor disproved, and Rochette et al.(2004) showed that the emissions associated with N-fixing crops could be considerably smaller that those predicted by IPCC default emission factors.

The majority of researchers report large variability of N_2O fluxes even for a given crop type, with large uncertainty in estimates. For example, annual N_2O emissions varied within the range of 0.6 – 8.7kg N_2O-N ha^{-1} for corn (Goodroad et al., 1984; Cates and Keeney, 1987; Sehy et al., 2003; Drury et al., 2006; Wagner-Riddle et al., 2007) and 0.7 – 6.3kg N_2O-N ha^{-1} for alfalfa (Wagner-Riddle et al., 1996; Rochette et al., 2004; Dusenbury et al., 2008), with manure application substantially increasing the level of N_2O emissions from any crops. The difficulties in proper quantification of N_2O fluxes from agricultural soils and the detection of any regular emission patterns arise from both the large diversity of combined climatic and land conditions affecting flux formation as well as the highly variable and instantaneous, 'spike-like' nature of N_2O flux. Most N_2O flux responses to environmental changes or anthropogenic factors occur on the time scales of several hours to several days (Teepe et al., 2001). Therefore, continuous, high frequency, long-term monitoring of N_2O field emissions is essential for furthering our knowledge about N_2O formation and release.

Recent development of micrometeorological flux measurement methodologies has created an alternative to the traditional chamber methods (Laville et al., 1999; Edwards et al., 2003; Scanlon and Kiely, 2003; Pattey et al., 2006; Wagner-Riddle et al., 2007). Although more technically challenging and more expensive than chambers, micrometeorological monitoring is becoming popular for routine landscape-level N_2O determinations. It provides high precision, high frequency, fast response, real-time data suitable for precise flux estimates such as by eddy covariance, the most commonly used direct flux calculation approach.

To our knowledge, this study is the first comprehensive research on the long-term continuous eddy monitoring of N_2O flux from dairy manure-fertilized croplands in the Northeastern US. We present the results of eddy flux N_2O measurements from manure-fertilized croplands of the large dairy farm in New York State. The specific objectives addressed in this paper are: (a) to measure N_2O year-round emissions from alfalfa and corn manure-fertilized fields using eddy covariance methodology; (b) to identify the annual patterns of N_2O formation depending on climate conditions and manure applications; (c) to estimate the magnitude of fertilizer-induced N_2O emission factors and compare those with predicted IPCC-based values.

2.2 Materials and methods

2.2.1 Experimental site

The selected research sites were located at Cornell University Animal Science Teaching and Research Center (abbreviated T&R), Harford, NY, USA (42^{o}26"N, 76o15"W). The T&R farm has 526ha of cropland in corn and alfalfa with ~750 head of dairy cattle and represents a large dairy farm with cropping practices typical for New York State. The T&R Center is geographically located in the Appalachian Plateau region; its landscape consists of uplands cut by valleys from north to south with elevation ranging from 360m on the valley floor to 520m in the uplands. Unconsolidated deposits of gravel, sand, silt, clay and till underlying the soils become saturated nearly to the land surface during spring time, and the groundwater table intersects the ground surface near 370m contour line. Upland originated streams have the maximum flow during spring snowmelt and often dry out in summer. This intermittent nature is indicative for small watersheds with low moisture storage in the upland soils (Swader, 1974).

Our monitored sites were located on the north-eastern and north-western parts of the valley at the elevation of 375-380m, relatively close to the valley floor and water table (Figure 2.1). The soils on the research sites were well-drained Howard gravelly loam (loamy-skeletal, mixed, active, mesic Glossic Hapludalfs) with 12.0% clay, 45.3% sand, 42.7% silt and 4% organic matter.

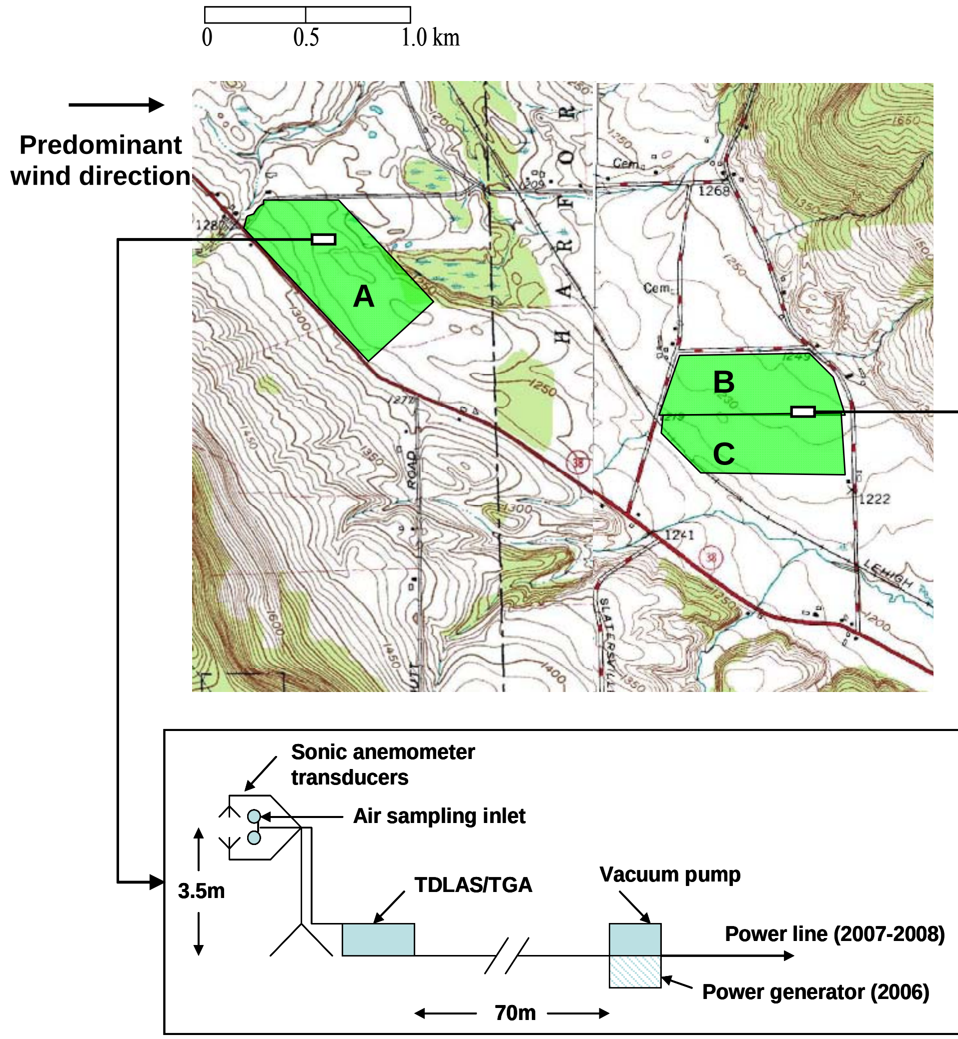

Figure 2.1. Topographic map of Cornell Teaching and Research Center at Harford, NY, USA (42°26'N, 76°15'W) and the locations of eddy covariance monitoring setup: A – under alfalfa in 2006; B – under corn in 2007 and 2008; C – under corn in 2007 and under alfalfa in 2008

The observations of N_2O flux were carried out during years 2006, 2007 and 2008 on two fields. The first was an alfalfa field monitored during growing season of 2006. In 2007, the experimental system was moved to the second field where corn was planted. Monitoring continued at the same site in 2008, when approximately a half of the field area was rotated to alfalfa whereas the remainder stayed in corn. General information about the sites is given in Table 2.1. All sites were tilled: moldboard plowed (corn) or chiseled followed by disc harrowing (alfalfa) before planting in early spring.

2.2.2 Manure fertilization

The fields received fresh semi-solid and/or liquid dairy manure annually, with the schedule of application determined by crop and tillage type and farm manure management needs. Manure was surface broadcasted for up to 12 weeks each year without immediate incorporation. The application schedules and amounts of applied manure varied largely from year to year (Table 2.2). The alfalfa-2006 field received manure fertilization in summer/early fall of 2006, immediately following the harvest, with the monthly peak manure load of 70 wet tons ha^{-1} in July. About 87% of alfalfa fertilization was in form of the liquid slurries, with the volume of manure water contributing to the high soil moisture contents in the already-wet summer 2006. The corn-2007 field was fertilized in winter/early spring on the top of snow cover, and the monthly peak load of 176 wet manure tons ha^{-1} was applied in January. The alfalfa portion of the split alfalfa/corn site in 2008 was fertilized in winter/spring with the monthly peak of 83 wet manure tons ha^{-1} occurring in March; the corn portion of the same site received total of 65 wet manure tons ha^{-1} in May.

Amongst all, the corn-2007 site received the largest total manure load, and the corn part of split field in 2008 was the least fertilized, with the difference in about an order of magnitude. Table 2.2 shows manure spreading dates, amounts and manure characteristics for all sites. The monthly manure N loads varied from the lowest of 7kg ha^{-1} of total manure N in September 2006 to the highest of 557kg ha^{-1} of total manure N in January 2007 (Figure 2.2). Total manure nitrogen and total ammoniac nitrogen accounted for up to 0.44% and 0.18% of the wet manure weight, respectively.

Table 2.1.General information about research sites at Cornell T&R Center monitored for N_2O-N emissions in 2006-2008

Monitored site	**Period of observations**	**Field area, ha**	**Plowing times**	**Harvest times**
Alfalfa -2006	20 Apr – 10 Oct 2006	24.8	-	10 Jun, 31 Jul, 31 Aug 2006
Corn -2007	1 Dec 2006 – 31 Dec 2007	29.7	23 -31 Mar, 2007	5 Oct 2007
Split alfalfa/corn - 2008	1 Jan – 31 Dec 2008	29.7 (14.1 alfalfa, 15.6 corn)	Alfalfa: 10-17 Apr, 2008 Corn: 9 May, 2008	Alfalfa: 9 Jul, 18 Aug 2008 Corn: 5 Oct, 2008

Table 2.2.The manure loads, application schedules and nutrient information

Monitored site		**Manure application periods**	**Total amount of manure applied, wet tons ha^{-1}**		**Total manure N applied, kg ha^{-1}**	**Total ammonia N applied, kg ha^{-1}**	**Total manure solids, tons ha^{-1}**	**Total P, kg ha^{-1}**	**Total K, kg ha^{-1}**
			Semi-solid	**Liquid**					
Alfalfa-2006		06.09.2006 – 09.30.2006	17.2	118.9	291	147	7.2	41	182
Corn-2007		12.22.2006 – 03.15.2007	318.5	2.0	1296	585	49.1	166	899
Split alfalfa/ corn - 2008	**alfalfa**	01.18.2008 – 04.10.2008	179.6	12.7	750	340	28.1	97	52
	corn	04.30.2008 – 05.14.2008	8.0	56.9	125	70	3.4	20	86

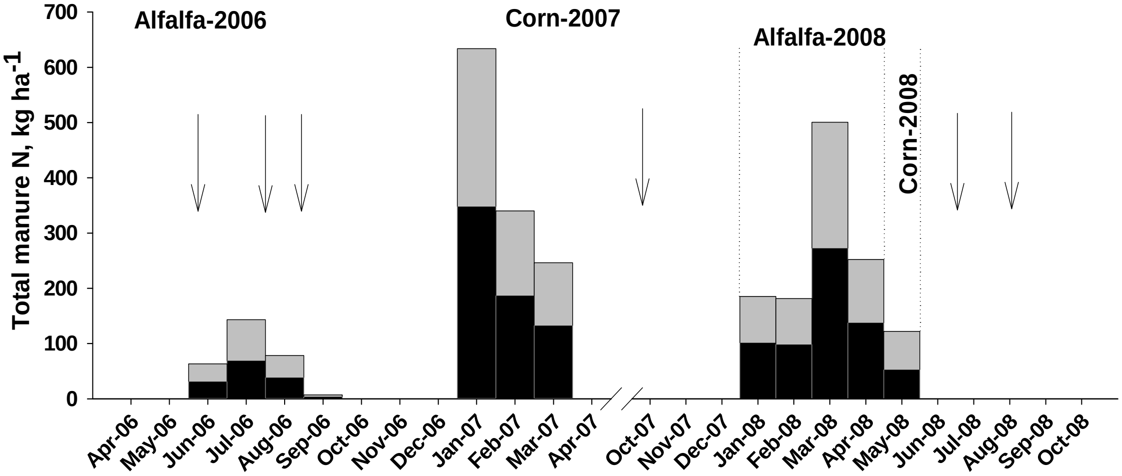

Figure 2.2. Monthly loads of manure total organic (black bars) and ammoniac nitrogen (grey bars) to the alfalfa, corn and split alfalfa/corn fields in 2006-2008. Arrows indicate the harvest dates

Noticeably, the amount of field applied manure N was not consistent from year to year and sometimes largely exceeded N-recommendations for the crops (Ketterings et al., 2003). However, the situation could be reflective of dairy farms that do not have manure storage facilities and need to dispose collected manure immediately. In such a case, controlling manure application rates can be more difficult, with overfertilization potentially leading to much greater emissions.

2.2.3 Instrumentation

Eddy covariance determinations require accurate high resolution three-dimensional wind speed and nitrous oxide concentration measurements. Wind speed measurements were conducted with 3-D sonic anemometer (model CSAT3; Campbell Scientific, Inc.); the N_2O concentration was measured by Tunable Diode Laser Absorption Spectrometry/Trace Gas Analyzer (TDLAS/TGA) (model TGA100A; Campbell

Scientific, Inc.). The TGA sampling inlet and 3-D anemometer were mounted to the tripod mast at a height of 3.5 m, and oriented toward the prevailing wind direction.

The sample air was drawn through the N_2O sample cell under 50-55mbar with a rotary vane vacuum pump (R5 series; Bush, Inc.) installed 70m downwind from the TGA location. The laser operating temperature was 88.6^oK. The system was powered by a gasoline generator (with supplemental fuel tank) for 2006 and by line power thereafter. To remove excess moisture and dust from the sample air, a diffusive dryer with a disposable 10.0μm polypropylene inlet filter (changes twice monthly or as needed) was installed between the sample intake and the TGA. A certified standard reference gas (2000ppm N_2O) simultaneously passed through the reference cell for continuous calibration. The measurement frequency was 10Hz, with half-hourly fluxes calculated from the high frequency data. The lag time for air travel between the sample intake and sample cell N_2O detector was calculated to synchronize time series between N_2O concentration and wind speed determinations. All data were collected using data logger (model CR5000; Campbell Scientific, Inc.) and standard compact flash card.

Data control was conducted in two steps. The first step was eliminating bad half-hour data averages related to technical shutdowns, interruptions and routine laser maintenance (data corresponding to TGA internal pressures of less than 45mbar or more than 60mbar, and TGA laser temperature more than 88.6ºK). The second step of data quality control prior to the eddy flux calculations included discarding of vertical wind speed standard deviations less than 0.1m s^{-1} and periods when overall wind direction angles were greater than 120^o from the bearing of the sonic anemometer. Covariances were rotated to a natural coordinate system. The “clean” half-hour flux data were then averaged to the daily and monthly means. The data filtering resulted in 51% of quality assured data in 2006, 72% in 2007 and 69% in 2008. More frequent downtimes due to generator failures or maintenance needs contributed to the lower fraction of assured data in 2006.

2.2.4 Weather and soil measurements

The experimental setup also included a number of sensors to continuously measure weather parameters (Figure 2.3) including air temperature and humidity (HMP45A/D probes; Vaisala Group) and precipitation (tipping bucket rain gauge). Data also collected but not reported here included net radiation, water vapor and carbon dioxide concentrations, and soil heat flux. The estimates of the source area contribution from alfalfa and corn parts of the field in 2008 were done using three-dimensional sonic wind speed measurements (U_x, U_y, U_z), and wind direction angle (η) calculated in relation to the sonic axis of CSAT3 anemometer.

High-frequency volumetric soil moisture content (CS616 Water Content Reflectometer, Campbell Scientific, Inc.) and soil temperature (thermocouple probes) measurements were added to the setup in December 2006 and July 2007, respectively. The CS616 reflectometer was field-calibrated by the standard soil-core gravimetric method and calibration coefficient was determined from a curve fit of known water content and sensor output.

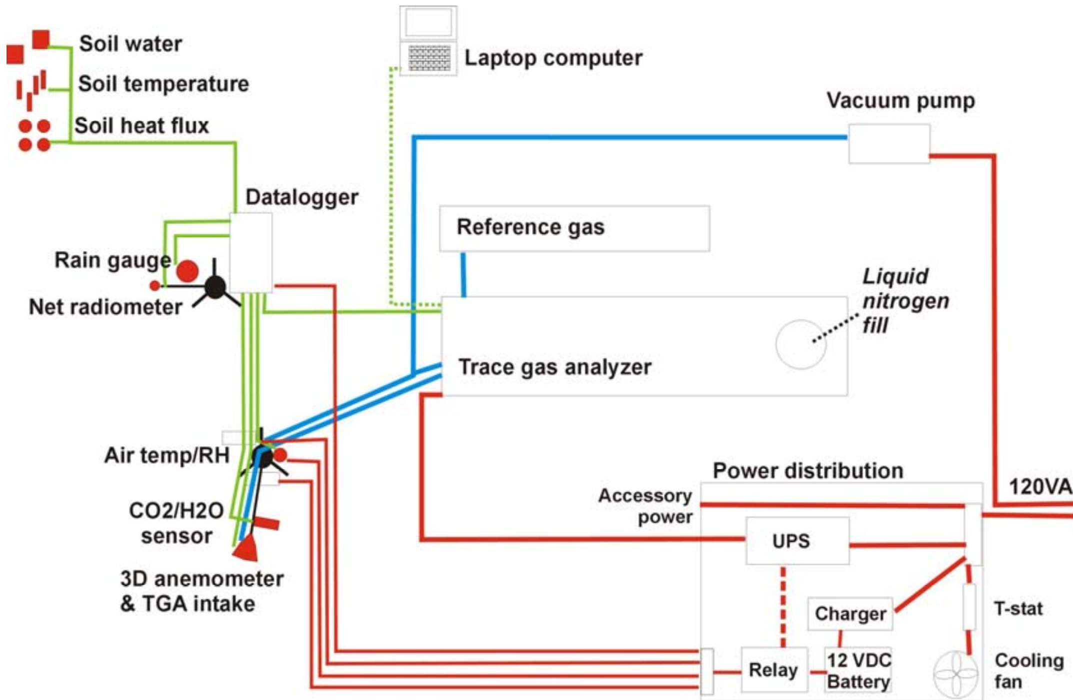

Figure 2.3. The scheme of experimental setup for eddy covariance greenhouse gas and weather monitoring at Cornell T& R Center, Harford, NY

Soil samples were collected bimonthly from May to September in 2006 and monthly from April to December in 2007–2008 on each site from the surface 10cm of soil using a 5-cm diameter aluminum soil core. The samples were refrigerated at 4^{o}C before analysis. NO_2/NO_3-N concentrations were determined after extraction with 2*M* KCL. For extract preparation, 5g of the field-moist soil was placed in centrifuge tubes with 50mL of 2*M* KCl, stoppered, shaken for 30 min, centrifuged at 3000rpm for 40min and filtered through 0.45m membrane filters (Pall Life Science Corp., East Hills, NY). The supernatant was analyzed for NO_2/NO_3-N colorimetrically by sulfanilamide method with continuous flow spectrophotometer (Astoria Analyzer; Astoria Pacific, Inc.). Gravimetric moisture content and bulk density was determined by drying for 24h at 105^{o}C, and the % of water filled pore space for alfalfa-2006 was calculated using those parameters.

2.2.5 Calculations and data processing

The eddy flux of N_2O was calculated directly from the vertical wind velocity and N_2O gas concentration, using the equation (Pattey et al., 2006):

$$F_S = \overline{\rho_a} * \frac{M_{N_2O}}{M_a} * \overline{w'c'} \qquad 2.1,$$

where F_S is the N_2O flux (μg m^{-2} s^{-1}), ρ_a is the dry air density (g m^{-3}), M_{N_2O} is the molecular mass of N_2O (g mol^{-1}), M_a is the molecular mass of dry air (g mol^{-1}), w is the vertical wind velocity (m s^{-1}), and c is the N_2O mixing ratio (concentration) in the air (μmol mol^{-1}). Flux calculations and data processing and filtering were carried out using Matlab, version 7.0 (The MathWorks, Inc.). The data gap filling for single data points was done by linear interpolation between two adjacent values. For more than one missing consecutive data points, however, no gap filling was done since due to the episodic nature of N_2O flux and lack of quantitative relationships which allow to substitute environmental factors for N_2O flux, gap filling is likely to introduce errors to emission estimates. Therefore, cumulative monthly N_2O emissions and emission factors represent lower bounding estimate for the amount of released N_2O.

The observation-based emission factors were calculated using updated IPCC methodology (IPCC, 2006) with the formula that accounts for direct N inputs from manure N and crop residues. The crop N residue input was calculated by using the default values for the above and below-ground residues dry matter and N content for alfalfa and corn were used, thus including the factor of different cropping practices into calculations. The significance of correlations between N_2O flux and environmental parameters (*P<0.05*) was tested by linear regression analysis.

2.3 Results

2.3.1 Climate conditions

Amongst the three years of observations, the 2006 was characterized by the greatest amount of precipitation during growing season, from April to October, to the extent that an ephemeral pond formed in a mid-field depression downwind from the sampling area. Total growing season rainfall in 2006 was 700mm (1142mm annual), whereas for 2007 and 2008 it did not exceed 481mm (895mm annual) and 438mm (833mm annual), respectively. For each year, the amount of rain reached its maximum during June-July (Figure 2.4a). Generally, spring and fall had less rainfall than summer, with the peaks usually around March and November. Heavy rainfall in summer 2006 resulted in the highest soil moisture content for all seasons that reached its peak of 91% water filled pore space (WFPS) in July. Soil water contents for 2007 and 2008 were much lower and ranged from 45% to 65% WFPS (Figure 2.4a), with the peak value in November-January (60-65%), drop in February-March (45-57% WFPS) and another rise in April (59-60% WFPS), associated with the spring soil thawing.

In 2006, 2007 and 2008, the average growing season temperatures for the research sites were 16.7, 14.3 and 13.9^{o}C, respectively. The 2006 growing season average was greater and the 2007 and 2008 ones were lower than the 10-year average for the area (15.0^{o}C). The warmest months were July in 2006 and 2008 (21.5^{o}C and 19.9^{o}C, respectively), and August in 2007 (19.2^{o}C) (Figure 2.4b). The soil temperature measurements were added in the midst of summer 2007 and generally showed slightly greater levels than air temperature, but their averages were still within the deviation

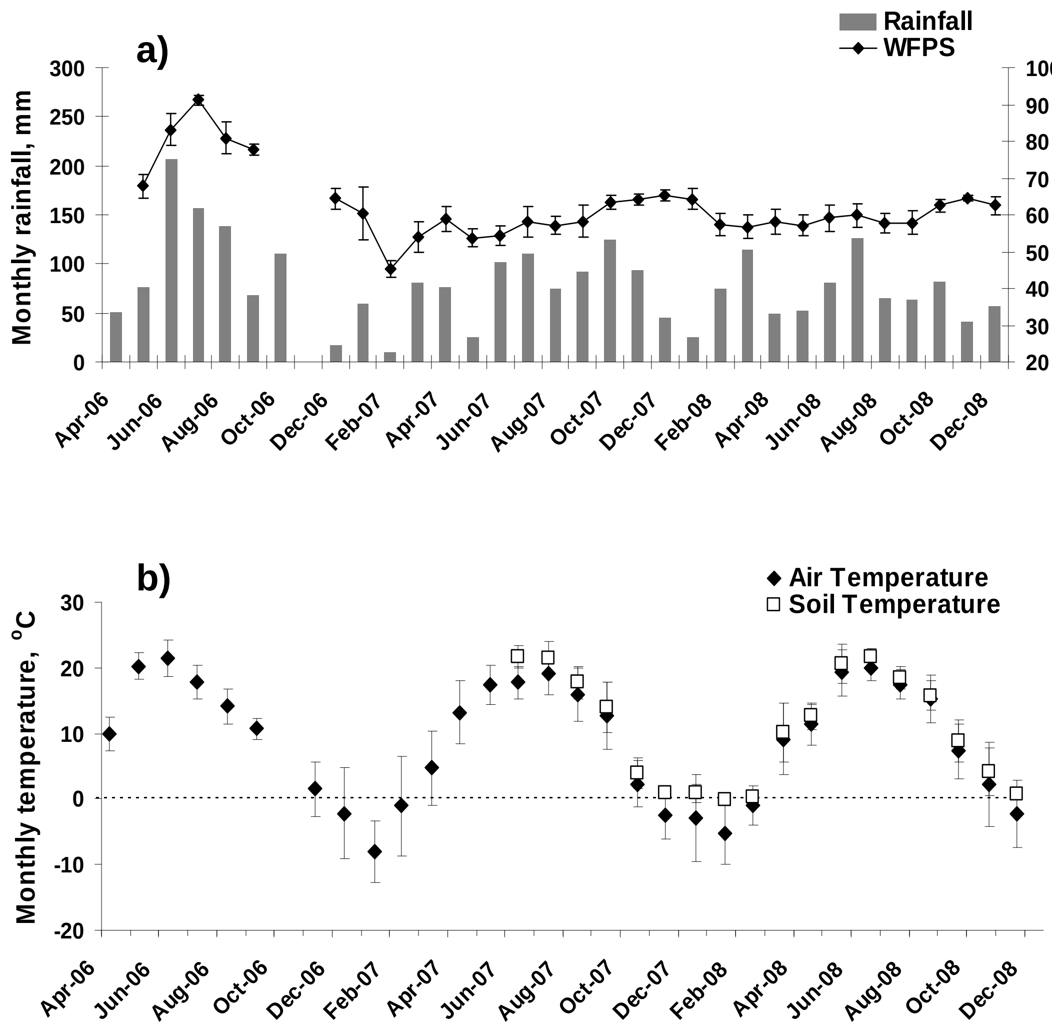

Figure 2.4. Climatic data from 2006, 2007, 2008 years of observation: a)monthly rainfall and soil moisture content; b) monthly air and soil temperature

values of mean air temperatures. The few exceptions were the winter months when even though air temperature dropped below freezing, soil temperatures remained above or around 0^{o}C (Figure 2.4b).

2.3.2 Soil nitrogen

The analysis of soil NO_2/NO_3-N content showed the greatest concentrations soon after or during fertilization events (Figure 2.5). In 2006, the peak soil NO_2/NO_3-N was observed in July; and the 2007-2008 soil samples both had peak NO_2/NO_3-N contents in April-May. Soil mineral N generally decreased by the end of the growing season after crop N uptake had occurred. The soil mineral N load among all sites generally reflected the amount of applied manure with the greatest and the lowest NO_2/NO_3-N contents observed for corn in 2007 and the corn part of the split field in 2008, respectively.

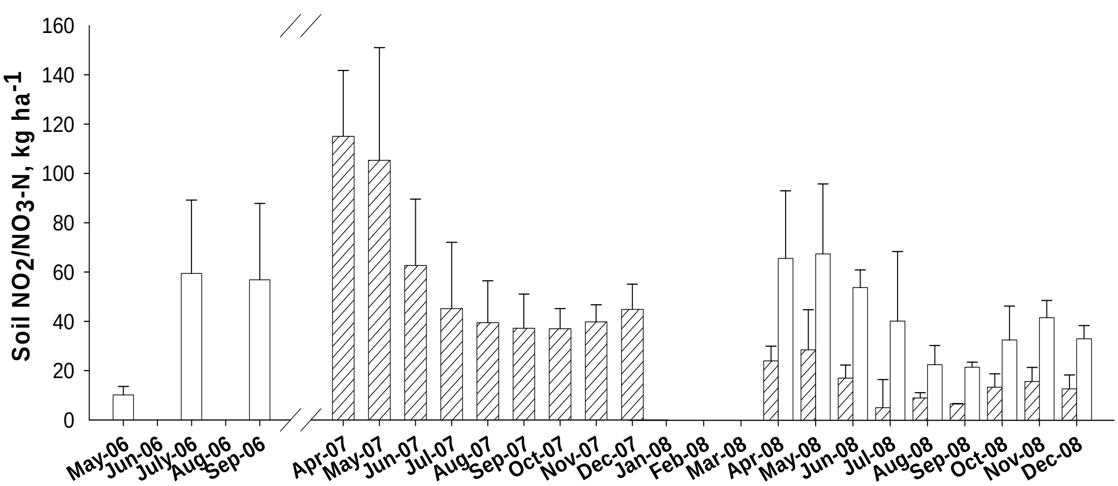

Figure 2.5. Monthly (bimonthly) soil NO_3/NO_2 –N concentrations from alfalfa (open bars) and corn (shaded bars) fields.

2.3.3 Total N_2O emissions and emission sources

Average monthly N_2O-N fluxes (Figure 2.6) for all three years of monitoring ranged from the lowest of -0.4 to the greatest of 108.4g N_2O-N ha^{-1} day^{-1}. The magnitude of N_2O-N flux strongly varied between the years. The 2007 season was characterized by the greatest absolute flux value amongst all: 34.9 and 54.0g N_2O-N ha^{-1} day^{-1} as for annual and growing season average, respectively. The alfalfa-2006 site showed slightly lower flux during the growing season of 30.5g N_2O-N ha^{-1} day^{-1} (no annual data). For the alfalfa/corn field in 2008, the absolute flux values were the lowest of all, 11.8 and 14.9g N_2O-N ha^{-1} day^{-1} for annual and growing season average, respectively. Non-growing season months (November-March) in 2007 and 2008 mostly showed low levels of emissions (-0.4 to +5.0g N_2O-N ha^{-1} day^{-1}).

Cumulative emissions were 3.24kg N_2O-N ha^{-1} for the growing season of alfalfa in 2006; 9.73 and 9.06kg N_2O-N ha^{-1} annually and for the growing season from corn in 2007; and 3.6 and 2.3kg N_2O-N ha^{-1} annually and for the growing season from split field in 2008, respectively. The temporal pattern of the flux distribution showed that for all sites the N_2O-N fluxes reached maxima during or immediately after manure fertilization events combined with seasonal weather changes.

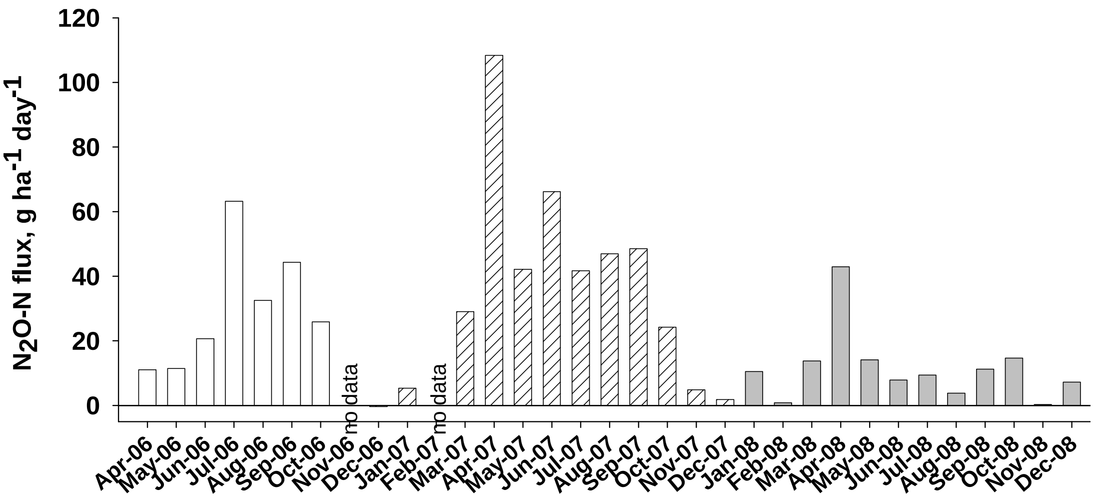

Figure 2.6. Monthly N_2O-N fluxes from alfalfa-2006 (open bars), corn-2007 (shaded bars), alfalfa/corn-2008 (grey bars)

The analysis of emission source areas for alfalfa/corn split field in 2008 based on wind direction calculations showed that corn and alfalfa fields contributed unequally to the overall emission level. The alfalfa portion of the field was the major contributor to the integrated flux approximately two thirds (64%) of the observation period, while corn was responsible for 36% of that time. Alfalfa's contribution was greater not only due to prevailing wind directions but also due to greater flux rates of emitted N_2O-N. Cumulative N_2O-N emissions in 2008 from the alfalfa field were 3.0kg ha^{-1} (mean daily rate of 17.3g ha^{-1} day^{-1}) in contrast to only 0.6kg ha^{-1} cumulative annual flux from corn (6.8g ha^{-1} day^{-1} mean rate). The alfalfa field also produced more high peaks: 89% of total daily fluxes over 100g N_2O-N ha^{-1} day^{-1} and 75% of daily fluxes between 50 and 100g N_2O-N ha^{-1} day^{-1} were recorded on days when winds were coming from the alfalfa portion.

2.4 Discussion

Nitrous oxide fluxes observed in this study were comparable to other eddy-covariance flux measurements in the literature (Skiba et al., 1996; Laville et al., 1999; Scanlon and Kiely, 2003; Di Marco et al., 2004; Hsieh et al., 2005), which generally exceed fluxes reported from chamber-based studies (Cates and Keeney, 1987; Sehy et al., 2003; Rochette et al., 2004; van Groenigen et al., 2004; Drury et al., 2006; Dusenbury et al., 2008). This could be due in part to the much higher frequency of eddy-covariance sampling which diminishes the risk of missing peak events that can account up to 50% of total annual emissions (Parkin, 2008). Contributing to the high flux values at our sites was elevated manure N loadings in contrast to lower N loading rates in other studies, in most cases less than or equal to 200kg N ha^{-1}.

2.4.1 Manure N loading effects

Our data suggest that manure N loading was the most important factor controlling the extent of N_2O-N flux formation, with fluxes reaching maxima during or immediately after spreading events. The magnitude of each annual maximum (63.2g N_2O-N $ha^{-1}d^{-1}$ in July for alfalfa-2006, 108.4g $ha^{-1}d^{-1}$ in April for corn-2007, and 43.0g $ha^{-1}d^{-1}$ in April for alfalfa/corn-2008) substantially exceeded the next highest monthly average of any given year by at least 30%, which is in agreement with the previous observations that instantaneous event-caused releases of N_2O-N are major contributors to total annual emissions (Scanlon and Kiely, 2003; Parkin, 2008).

The variability in the absolute flux values amongst the three years of observations was most likely caused by the large variation in annual manure applications (Table 2.2), which can be somewhat compensated for by normalizing the absolute N_2O flux value as a fraction of manure N applied. Resulting percentage for 3-month periods (Figure

2.7) demonstrate that even though corn-2007 was characterized by the greatest N_2O-N absolute flux values, the relative emissions from alfalfa-2006 in July-September and October-December (1.47% and 0.28%, respectively) exceeded all others as the percentage of applied manure N.

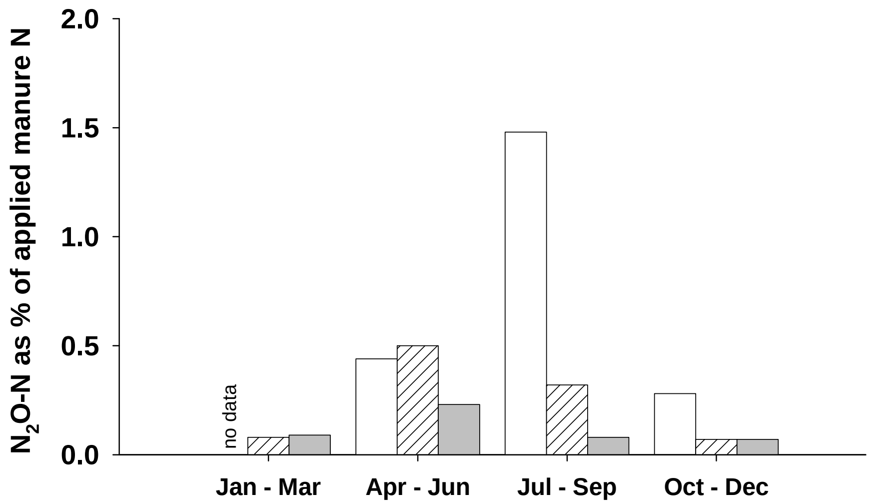

Figure 2.7. The fraction of total applied manure N emitted as N_2O-N calculated for three-month periods from alfalfa-2006 (open bars), corn-2007 (shaded bars), split alfalfa/corn-2008 (average of the two, grey bars)

The July-September alfalfa flux value was also the greatest of all observed periods, driven not only by the intensive manure N application, but also high soil moisture contents and warm soil conditions. Lowest levels of N_2O emissions both in absolute units and as % of applied N were observed in 2008 resulting from the lower manure load, drier conditions and milder winter temperatures.

2.4.2 Soil moisture and temperature effects

Almost all high N_2O-N flux events were observed as a result of manure application and/or pronounced changes in weather conditions. In 2006, the alfalfa field was primarily fertilized during the summer, which was characterized by heavy rainfall (resulting in very high soil moisture contents of 78 to 91% WFPS), and greater than average summer temperatures, resulting in the greatest 2006 peak of N_2O-N observed in July (Figure 2.5). The contributions of both nitrification and denitrification to N_2O-N emissions following summer manure spreading appear to be significant: the substantial manure ammonium content (Table 2.2) under warm temperatures supports nitrification with generation of N_2O as a byproduct (e.g. Molodovskaya et al. 2008). Production of nitrate in combination with repeated rainfall events and elevated soil moisture (leading to temporally-variable saturation extents) would thus support substantial denitrification and N_2O production as well.

For both 2007 and 2008, winter manure applications were followed by spring thaws and high N_2O emission peaks in April of each year resulted from the combination of those two events. Early spring N_2O emission peaks, which can account for up to 70% of the annual flux (Kaiser et al., 1998; Röver et al, 1998), are typically associated with rising soil temperatures and snowmelt-induced increases in soil moisture that together induce denitrification (Mørkved et al., 2006). Soil water contents of 50 to 90% WFPS provide incomplete denitrification and consequent N_2O release (Smith et al., 1998; Sey et al., 2008, Singurindy et al. 2009). In 2007-2008, soil moisture generally remained within the range of 54 to 64% WFPS, with the only exception being a sharp increase from 45% to 58% WFPS in February-April 2007 (Figure 2.4a). This increase coincided with manure application and a rise in temperature from -8 to +5^{o}C (Figure 2.4b) that together triggered the greatest N_2O-N monthly value observed in the study (Figure 2.6) which accounted for ~21% of 2007 emissions.

In contrast, the spring thaw of 2008 was less dramatic: soil moisture remained near 60% WFPS, and, partly due to warmer average January-February air temperatures in 2008 (-5.2 vs. -8.0^{o}C in 2007), the soil temperature rarely dropped below freezing (Figure 2.4b). The highest annual N_2O peak however was still observed in April 2008, following the manure N fertilization and temperature rise (from -5.2 to +9.1^{o}C). It contributed ~31% of the 2008 emission, but accounted for only 0.15% of applied manure N, in contrast with 0.25% for the April 2007 peak. Similar results were reported by Regina et al. (2004), when the lack of a significant spring thaw event resulted in lower emissions. The observations of Wagner-Riddle et al. (2007) based on the 5 year long monitoring of agricultural fields also proved that milder winters with reduced soil freezing in general produce lower spring N_2O fluxes.

With the exception of the 2007 spring thaw, there was no overall correlation between soil moisture changes and N_2O flux formation on a monthly scale, and, similar to the findings of Venterea et al. (2005), soil moisture contents apparently neither limited nor promoted N_2O production. In the absence of sharp soil moisture fluctuations, temperature and manure N application appeared to be the major regulators of emissions. A positive correlation was observed between the monthly mean N_2O flux values and NO_3/NO_2 –N soil concentrations (Figure 2.8), supporting the conclusion that N inputs were the primary drivers of N_2O formation (the correlation analysis included only data with monthly temperatures >5^{o}C, to exclude periods when denitrification could be limited by low temperatures).

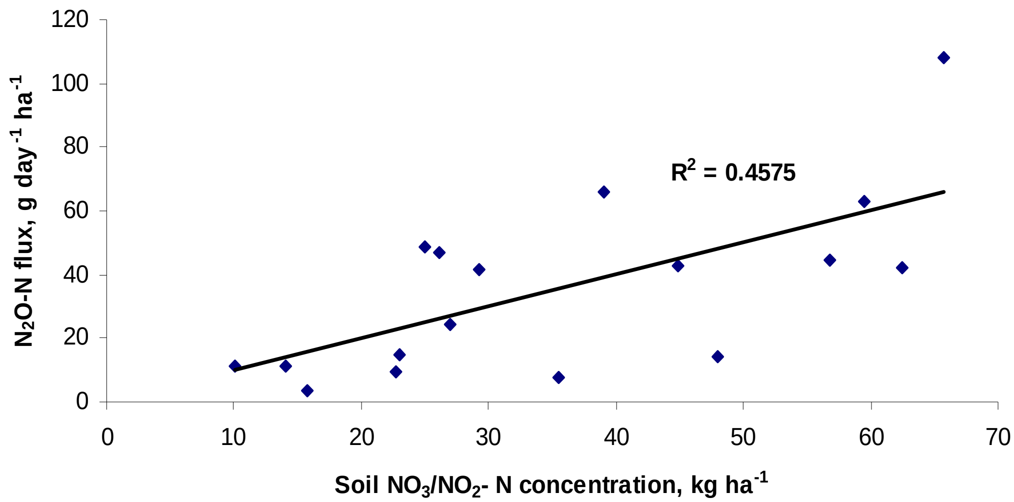

Figure 2.8. N_2O-N fluxes as related to the soil NO_3/NO_2-N content from 2006-2008 at soil temperatures ToC >5oC

Denitrification was likely responsible for the secondary annual flux increases observed after harvest in September-October on all sites (Figure 2.6), when the cessation of crop N uptake led to higher levels of mineral soil N (Figure 2.5) available for denitrification.

2.4.3 Split field alfalfa vs. corn contributions

The concurrent monitoring of the split alfalfa/corn field in 2008 showed substantial differences in the contributions of the respective crop footprint areas to the integrated EC flux. Obviously, this difference resulted from the integrated effects of fertilization and cropping practices and cannot be attributed solely to the crop type. Although the predominance of the alfalfa footprint contribution to the integrated flux above that of corn was observed throughout the year, the majority of the high peaks (>100g N_2O-N ha^{-1} day^{-1}) were reported during April 1-20, when that part of the field which would subsequently be planted with alfalfa was plowed. The combined effects of plowing, abrupt temperature rise, and recent fertilization together triggered a strong N_2O-N spike from the field before the beginning of growing season and thus independently of the crop choice. The corn section of the field was not plowed until May 9, well past the spring thaw peak, which could have moderated N_2O-N release as compared to the alfalfa portion. The observed greater alfalfa N_2O-N fluxes including those during growing season were probably due to greater fertilization rates (Table 2.2) and the lower N uptake by the new (and leguminous) alfalfa stand (Ketterings et al. 2008), leaving more mineral N remained available for denitrification. With the manure amounts and magnitude of N_2O response highly variable between all three sites, it is not clear how agricultural practices alone affected total emission levels. Detailed determinations of individual crop effects on N_2O emissions would require more uniform and controlled fertilization and land treatment conditions, a task for future studies.

2.4.4 Emission factors

The emission factors (EF) for all three years of observations were calculated using the updated IPCC methodology (IPCC 2006) which includes manure N and crop N residue inputs. The annual EF values for corn-2007 and corn/alfalfa-2008 were 0.75% and 0.62%, respectively, and were below the IPCC default EF of 1.00% (for non-organic soils). Due to the lack of annual data, the 2006 EF was calculated only for growing season. Nevertheless, growing season EF of 1.11% in 2006 exceeded both the default IPCC value and annual EFs for 2007 and 2008, even though the absolute N_2O fluxes were greatest in 2007. Observation-based EF values can thus be strongly affected by local climate factors (such as summer manure spreading accompanied by the strong rainfall), which has to be accounted for along with N inputs and land use when modeling N_2O emissions.

2.5 Conclusions

The results of continuous eddy covariance monitoring of N_2O from manure amended corn and alfalfa fields during 2006-2008 showed high seasonal variability of N_2O fluxes. The emissions were strongly influenced by manure N loads and manure application timing. All test fields produced their greatest N_2O levels within the month following manure application: alfalfa field in July 2006, corn in April 2007, and split alfalfa /corn field in April 2008, respectively. Summer emissions were enhanced by strong rainfall combined with warmer than average temperatures, whereas winter emissions were promoted by spring thaw periods. Summer manure spreading on alfalfa field resulted in the greatest emission factor, which also was higher than default IPCC value, even though the absolute flux values were greatest for the winter-fertilized corn field. The contribution of climatic parameters to fluctuations of EF values thus can be significant, however their direct effect is not clear and more annual data from continuous monitoring of those crops is needed for statistically reliable estimates.

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CHAPTER 3

MEASUREMENTS OF AGRICULTURAL NITROUS OXIDE EMISSIONS: A COMPARATIVE STUDY OF STATIC CHAMBER AND EDDY COVARIANCE FLUXES

3.1 Introduction

Agricultural practices, especially those related to N fertilization, are believed to be the greatest anthropogenic contributor to the steady increase in atmospheric nitrous oxide (N_2O) (Kroeze et al., 1999) which is of concern given its persistence, its role in ozone depletion and its high CO_2 equivalence (310 CO_2 eq.). Substantial recent effort has gone into the development of reliable and robust tools for N_2O emission measurements, but uncertainty still exists in modern data sets, mainly owing to the high spatial and temporal heterogeneity of N_2O net production as well as limitations of current methodologies. Two major groups of methods - each with its own methodological niche, advantages and limitations (Denmead, 2008) - are generally considered for N_2O flux measurements from agricultural soils: 1) ground-based conventional chamber techniques and 2) micrometeorological methods. For many years, chamber techniques had almost no viable alternative and provided relatively inexpensive and reliable soil N_2O measurements, which formed the basis for our current understanding of N_2O emissions. Regular chamber measurements of soil N_2O coupled with GC/ECD analysis began in the 1970s and 80s (Delwiche and Rolston, 1976; Dowdell and Cress, 1974; Rolston et al., 1978; Ryden et al., 1978; Hutchinson and Mosier, 1981) and continue to date (e.g., Sehy et al., 2003; Rochette et al., 2004; van Groenigen et al., 2004; Venterea et al., 2005; Yates et al., 2006) based on the same methodological principles, although chamber designs and deployment protocols have been significantly improved (Hutchinson and Livingston, 2001; Rochette and Eriksen-

Hamel, 2008). Closed non-steady state chambers are the most common for the process-level study of N_2O flux formation caused by microbial and/or chemical soil interactions. The limitations of using chambers are mainly related to the poor representativeness of temporal and spatial flux variability due to the low sampling frequency, small footprint areas (usually less than 1 m^2), and disturbances of the soil environment and land/atmosphere interactions caused by the chamber collars and closures (Denmead, 2008). Although increasing sampling frequency and chamber density can substantially improve low temporal and spatial resolution of data, it involves additional labor inputs, which is often a limited resource.

As an alternative to chamber techniques, micrometeorological methods for greenhouse gas measurements have been rapidly developing for the last two decades (Fowler et al., 2001; Edwards et al., 2003; Pattey et al., 2007). In contrast to chambers, micrometeorological instrumentation does not disturb the soil ecosystem and allows flux monitoring from a much larger source footprint area. One of the micrometeorological techniques widely used for N_2O measurements is eddy covariance (EC), which is based on direct flux calculations from instantaneous changes in vertical wind speed and trace gas concentration in the air above the soil surface (Stull, 1988; Baldocchi, 2003). Current eddy covariance equipment for N_2O flux monitoring includes a tunable diode laser absorption spectrometer (TDLAS) coupled with a 3-D sonic anemometer for N_2O concentration and wind speed measurements, respectively. The system design allows continuous operation providing high-frequency, fast-response real-time data suitable for estimates of N_2O flux temporal variability. The method is limited, however, by the requirements of horizontal fetch homogeneity (which requires careful site selection) as well as by stability of meteorological conditions. Atmospheric stability departing markedly from neutral can cause large deviations and random errors to the data, so extensive data quality checks are necessary to screen and verify the EC results. Unlike chambers, the EC method gives information on the integrated flux over a larger footprint but no particular insight into the localized variability of soil processes affecting N_2O formation. In addition, the application of the EC method is often limited by the considerable equipment expense. Nonetheless, micrometeorological methods and the EC in particular have lately become more common tools for routine N_2O flux observations and are being used for both short and long-term monitoring of agricultural N_2O (Wienhold et al., 1995; Hargreaves et al., 1996; Skiba et al., 1996; Wagner-Riddle et al., 1996; Laville et al., 1999; Scanlon and Kiely, 2003; DiMarco et al., 2004).

Since numerous studies carried out using different techniques are often synthesized into larger databases representing collective N_2O flux monitoring efforts (Bouwman et al., 2002; Stehfest et al., 2006; Flechard et al., 2007), it is important that data sets obtained by different methodologies be meaningfully comparable. To date few studies have focused on combining micrometeorological monitoring with simultaneous chamber N_2O measurements from agricultural lands under homogeneous treatments (Smith et al., 1994; Christensen et al., 1996; Laville et al., 1999) and reported good agreement (within STD range) between the two techniques. The EC flux, however, can be strongly influenced by changes in wind direction and any variety of treatments present within the footprint (Smith et al., 1994; Christensen et al., 1996), but data on how footprint heterogeneity may affect an integrated flux are scarce. Since chambers are the only tool currently available for estimating spatial variability of N_2O emissions at the field scale, parallel measurements with both techniques can be a useful tool to cross-validate both methods and identify the local sources of N_2O emissions, especially where heterogeneities of crops, soil conditions and/or other treatments may be present in the contributing area (Pattey et al., 2007). We thus carried out simultaneous chamber and EC measurements of N_2O flux from adjacent alfalfa (*Medicago sativa* L.) and corn (*Zea mays* L.) fields in the Northeastern US. This study was part of the long-term continuous EC monitoring of N_2O emissions that was conducted in 2006-2008 on manure-fertilized fields on a large dairy farm in the New York State (Molodovskaya et al., 2009). The main goals of this work were 1) to quantify micrometeorological N_2O flux from the mixed agricultural landscape; 2) to estimate small-scale N_2O fluxes from each treatment within the same footprint by static closed chambers; and 3) to analyze the contribution of each treatment to integrated emissions.

3.2 Materials and methods

3.2.1 Site description

The experimental site was an agricultural field located at Cornell University Animal Science Teaching and Research Center (T&R), Harford, NY, USA (42^{o}26'N, 76^{o}15'W, elevation 384m). The T&R Center is a large dairy farm with over 500ha of cropland under typical in New York State silage corn (*Zea mays*) and alfalfa (*Medicago sativa*). The landscape consists of uplands cut by valleys from north to south with elevation ranging from 360m on the valley floor to 520m in the uplands. The groundwater table intersects the ground surface near 370m contour line; and the watershed is characterized by low moisture storage in the upland soils with intermittent streams that have maximum flow during spring snowmelt and often dry out in summer. Annual 30-year average temperature and rainfall for the area were 7.8^{o}C and 932mm, respectively. The soils at the T&R Center are Howard gravelly loam (loamy-skeletal, mixed, active, mesic Glossic Hapludalfs), well drained, medium textured, with relatively high organic matter content.

The field site was continuously monitored for N_2O flux and weather data during 2007-2009; this study, however, describes a short term experimental campaign conducted from June 30 to July 3, 2008. Corn was planted over entire cropping area in 2006 – 2007, but in 2008, approximately half of the area (24.8ha) was rotated to alfalfa whereas the balance of the field (29.7ha) remained in corn (Figure 3.1). Fields were fertilized with dairy manure annually during winter and/or early spring. The manure was surface broadcasted without immediate incorporation. In 2008, manure applications were carried out daily during January 18 to April 04 for the alfalfa field and April 30 to May 14 for corn, with total loadings of 750kg N ha^{-1} for alfalfa and 125 kg N ha^{-1} for corn. The detail description of monitored sites including crop and manure practices is given by Molodovskaya et al. (2009). All fields were tilled (moldboard plowed for corn; chisel plowed for alfalfa) in early spring prior to planting.

3.2.2 Static chamber instrumentation and analysis

Easily-constructed and inexpensive chambers were designed, being composed of two parts: an opaque cylindrical collar (30cm diameter) made from the upper 17cm of standard “5-gallon” (19L) plastic buckets which was designed to be installed (wide-end down) in the soil, and a removable cover that fit over the collar and which consisted of a standard opaque 3.5-gallon (13.2L) plastic bucket (Paragon Mfg.) fitted with sampling and vent ports. A large rubber band (size 12G, 305cm long x 5 cm wide flat dimensions; Dykema Co., McKees Rocks, PA) was stretched around the outside of the upper portion of the collar to provide a gas-tight seal between collar and cover.

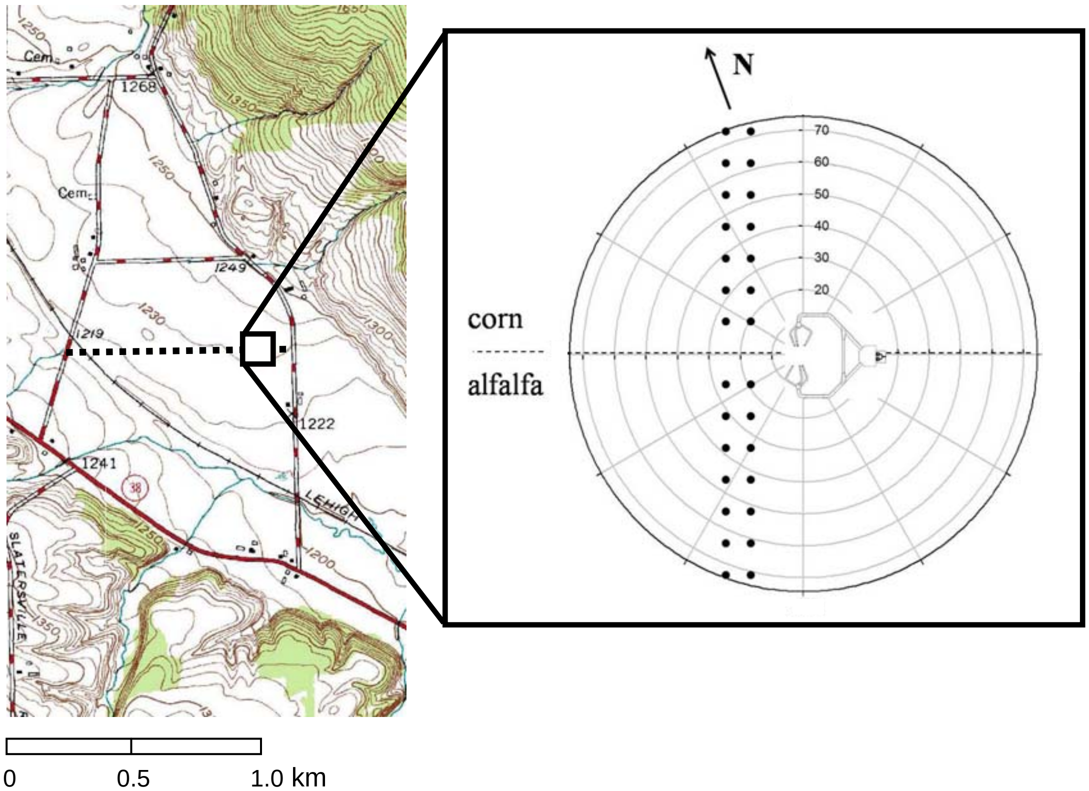

Figure 3.1. Topographic map of the Harford T&R Center (source: USGS Maps, 1949) and experimental setup of the static chambers (black dots) and micrometeorological equipment (center of the diagram) in the field. The distance between chambers is shown in meters.

Each cover top was equipped with a rubber serum bottle septum (to allow insertion of a gas sampling syringe) inserted in the center of the cover. A pressure equilibration vent tube (dimensions calculated from Hutchinson and Mosier (1981) equations) was inserted through a second septum 10cm from the gas sampling septum. The vent tube consisted of an aluminum pipe (1.1cm OD x 5.0cm L) fitted (on the inside of the cover) with an 18.5-cm length of 0.45-cm ID flexible plastic tubing. Leak tests were performed for each collar/cover pair before field installation using a gas leak detector (Model 21-250, Gow Mac Instrument Co., USA). Covers were installed on the collars only during actual sampling runs to minimize potential effects on the soil. Coverage area and enclosed volume of the closed chamber were $0.07m^2$ and $0.017m^3$, respectively.

The chamber N_2O campaign was conducted from June 30 to July 3, 2008, with three sampling deployments conducted each day at 11:00; 12:30 and 14:00. Twenty-eight static closed chambers were installed on a transect linking adjacent alfalfa and corn fields, with seven replicate pairs of chambers in each crop field (Figure 3.1). The distance between chamber sites along transects was 10m, and replicates were set within 30cm of each other. Collars were inserted 5cm into the soil one week prior to the deployment. Field deployment time for each chamber cover was 30 min, with four gas samplings taken at time 0, 10, 20 and 30min from the moment of closing. Duration of deployment and frequency of sampling were determined from chamber design and dimensions based the closed static chamber recommendations of Rochette and Eriksen-Hamel (2008). For alfalfa measurements, plants were present under the enclosure, whereas, due to crop height, chambers in the corn field were installed between the crop rows. Soil temperature was measured inside and outside chambers before and after each deployment. Air samples (10mL) were withdrawn through the septum with gas-tight glass chromatographic syringes (Hamilton Company, USA) and placed in previously evacuated (residual pressure < 100mbar), sealed and crimped Kimble® glass vials.

Samples were subsequently analyzed for N_2O concentration by gas chromatography using an Agilent 6890N GC/ECD (Agilent Technologies, Inc.,USA) equipped with a HP 7694 Headspace Autosampler (Hewlett-Packard Company, USA). N_2O separation was performed with a Supel-Q™ PLOT capillary column (30m x 0.32mm; Supelco Inc.) with ultra-pure He (20mL min^{-1}) carrier gas and 95:5 $Ar:CH_4$ make-up gas

(40mL min^{-1}), and 20:1 split injection. Operating temperatures were 100°C injection, -5°C column (using liquid N_2- cryogenic oven cooling to improve N_2O separation) and 360°C ECD-detector. Linear regression calibrations based on N_2O peak areas (Agilent ChemStation software) were prepared using a standardized N_2O gas (1ppm, balance N_2; Airgas, Inc., USA).

The N_2O flux measured by static chambers was calculated using the rate of change of N_2O concentration (*dG/dt*, mol min^{-1}) inside the chamber during 30min cover deployment (Rochette and Bertrand, 2007):

$$F_g = \frac{dG}{dt} * \frac{V}{A} * \frac{M_{N_2O}}{V_m} * (1 - \frac{e_p}{P}) \qquad 3.1,$$

where V is the chamber volume (m^3), A is the area covered by the chamber (m^2), M_{N2O} is the molecular mass of N_2O (44.0128g mol^{-1}); V_m is the molecular volume at chamber temperature and barometric pressure (m^3 mol^{-1}), e_p is the partial pressure of water vapor, (kPa), and P is the barometric pressure (kPa).

The rate of change in N_2O concentration (*dG/dt)* was estimated from the slope of the four-point concentration vs. time (time 0, 10, 20, 30) curve at t_0. In 75% of measurements, the curve fit the non-linear second-order polynomial equation ($y = ax^2 + bx + c$), which supports the theory that the concentration gradient decreases with time due to slowing gas diffusion inside the closed chamber (Mosier and Hutchinson, 1981; Yates et al., 2006, Rochette and Bertrand, 2007). In cases when only three-point concentration data were available, *dG/dt* was calculated as a slope of linear model ($y = ax + b$) as recommended by Rochette and Bertrand (2007). When N_2O concentration was decreasing with time (indicating soil N_2O uptake), *dG/dt* was also calculated using the linear model. The minimum detectable flux for the chambers determined from the standard deviation of GC/ECD analytical method and chamber dimensions (Parkin et al., 2003) was 0.2μg N_2O-N m^{-2} min^{-1}.

3.2.3 Eddy covariance instrumentation and analysis

The micrometeorological setup used for eddy covariance N_2O measurements is described in detail by Molodovskaya et al. (2009). The eddy flux was determined as the mean product of instantaneous vertical wind speed and gas concentration (Fowler, 1999; Laville et al., 1999; Pattey et al., 2006). A 3-D sonic anemometer (CSAT3; Campbell Scientific, Inc.) and TDLAS analyzer (TGA100A; Campbell Scientific, Inc.) were used to measure wind speed and N_2O concentration, respectively. The mast with sensors and air intake units was located between the alfalfa and corn fields; the sonic axis of 3-D sonic anemometer was oriented along the field dividing path (285° WNW) and coincided with prevailing wind direction in the area (Figure 3.1). The air sampling/wind measurements were performed at a height of 3.5m, and the lag time for air traveling between sample intake and N_2O detection was calculated to synchronize the N_2O concentration and wind speed time series. A diffusive dryer to remove water vapor and a disposable 10.0μm polypropylene filter to prevent dust from entering the analyzer were installed between the sample intake and TGA sample cell. High-frequency (10Hz) N_2O concentration and wind data was collected using a model CR5000 data logger (Campbell Scientific, Inc.). The detection limit of the EC measurements was calculated from standard deviation of vertical speed (σ_w) and the noise level (σ_c) of the TDLAS system (Pihlatie et al., 2005). For a 30min averaging period with 10Hz measurement frequency, the method's lowest detection limit was 0.05μg N_2O-N m^{-2} min^{-1}. Quality control was performed on the half-hour data prior to the covariance calculations (Molodovskaya et al., 2009). Covariances were rotated to a natural coordinate system. The data with friction wind velocity ≤ 0.1m s^{-1} and horizontal wind speed ≤ 1.5m s^{-1} were discarded to exclude measurements occurring when turbulent mixing was not sufficient (Laville et al., 1999). To remove potential disturbances to the wind from the equipment barn 60m behind the mast, data associated with wind directions ≥ 120^{o} and ≤ -120^{o} from the pointing direction of the sonic anemometer (azimuth of 45^{o}NE and 165^{o}SSE) were also discarded. The fluxes were averaged over half-hour and daily periods. Daily N_2O eddy fluxes were calculated for comparison with simultaneous chamber measurements. Minimum threshold for averaging half-hour to daily fluxes was 25% or 12 half-hour data points per day. All eddy covariance flux calculations and data processing were performed using Matlab, version 7.1 (The MathWorks, Inc., USA).

The wind direction angle (η) was calculated in relation to the sonic axis of CSAT3 anemometer from three-dimensional sonic wind speed measurements (U_x, U_y, U_z). High-frequency wind speed/ direction data were used to construct daily wind roses for the four days of the chamber and eddy measurements (WRPLOT View, version 5.9, Lakes Environmental Software). The source area contribution of the upwind area to the integrated flux was estimated by the model of Schuepp et al. (1990) as described by Laville et al. (1999), using the distance between the source and observation point. The footprint analysis showed that 40% of the flux originated within 75m of the EC system mast, and 75% of the flux originated within 150m of the mast.

3.2.4 Soil and weather parameters

The micrometeorological system included volumetric soil moisture content and soil temperature measurements. Two soil moisture sensors (CS616 Water Content Reflectometer, Campbell Scientific, Inc.) were installed at 10cm below the surface on the undisturbed (i.e. unplowed) part of the ground in ~5m from the mast. The measurements therefore represented background soil water storage. The reflectometers were field-calibrated by standard soil-core gravimetric method, with a calibration coefficient determined from a curve fit of known water content and sensor output. Soil temperature was monitored by four replicated thermocouple probes also installed at 10cm below the ground surface. Weather parameters included air temperature and humidity (HMP45A/D; Vaisala Group) and precipitation (tipping bucket rain gauge). All data were collected with 10Hz frequency, and averaged over half-hour periods (except for precipitation). Precipitation data were summed over the same time periods.

Soil mineral N content was analyzed for alfalfa and corn fields 24 hours prior to the chamber campaign. Soil samples were taken from five near-chamber locations on each field using an aluminum soil coring tool (10cm length, 5cm diam.). Soil NO_2/NO_3-N was analyzed by sulfanilamide method with continuous flow spectrophotometer (Astoria Pacific, Inc.). Soil NH_4-N content was analyzed fluorometrically using the o-phthalaldehyde (OPT) method. Gravimetric moisture content and bulk density were determined by drying soil core samples for 24 hours at 105^{o}C.

3.2.5 Statistical analysis

Daily mean N_2O fluxes and STD values were calculated for each chamber from three two-replicate deployments per day of measurements. Both EC and chamber fluxes were tested for normality with the K-S test (P=0.05), and corn/alfalfa and chamber/EC differences were analyzed using a parametric unpaired t-test or non-parametric Mann-Whitney rank sum test (SigmaStat 3.1, Systat Software). Descriptive statistical parameters (mean, median, maximum and minimum values, and coefficient of variation) for eddy covariance and chamber fluxes were calculated and compared for the period of chamber campaign.

3.3 Results

3.3.1 Eddy covariance and chamber N_2O fluxes

The eddy covariance data eliminated during screening were mostly attributed to nocturnal low-turbulence conditions between 20:00 and 05:00 or winds coming from behind the mast. The number of remaining quality-assured points varied from 14 to 29 out of 48 possible half-hour fluxes per day (Figure 3.2). The coefficient of variation (CV%) among half-hour EC fluxes was greater than for the chamber fluxes from either alfalfa or corn (Table 3.1) and reflected high temporal variability possibly resulting from the single point measurements and short averaging periods. The analysis of normality showed that EC fluxes were highly skewed and not normally

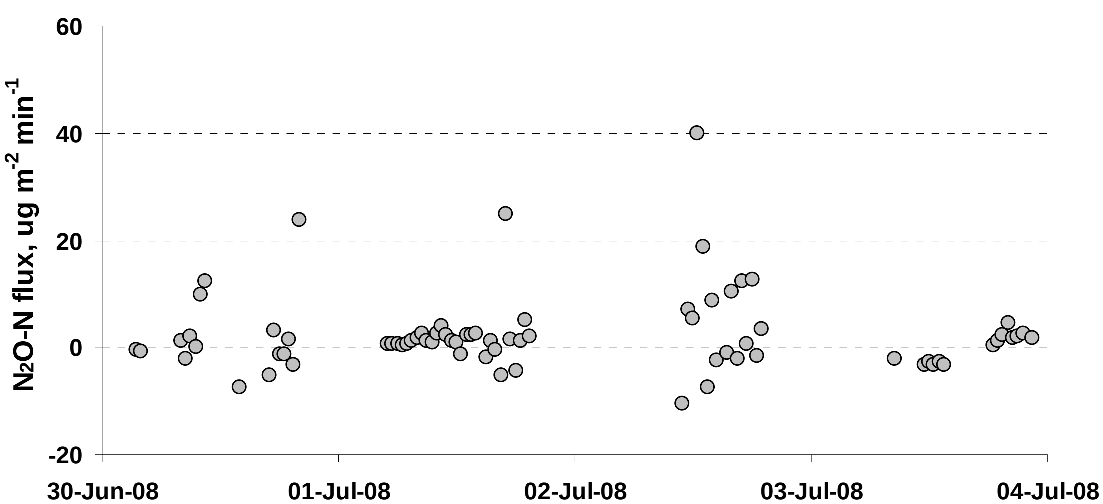

Figure 3.2.Half-hour N_2O-N fluxes measured by the eddy covariance method during June 29th – July 3rd, 2008

distributed (P<0.001) with the probability distribution being reverse J-shaped, as often observed for N_2O soil fluxes (Yates et al., 2006; Wagner-Riddle et al., 2007). The most scattered EC fluxes occurred on July 2, when both the greatest (40.0ug N_2O-N m^{-2} min^{-1}) and the lowest (-10.5ug N_2O-N m^{-2} min^{-1}) of all half-hour fluxes were documented (Figure 3.2). The same day was also characterized by the greatest daily mean EC N_2O flux of 3.4ug m^{-2} min^{-1}. The daily means for June 30, July 1 and July 3 were 2.2, 1.8, and -0.1ug N_2O-N m^{-2} min^{-1}, respectively.

Statistical analysis of chamber fluxes showed that both alfalfa and corn data were normally distributed (P = 0.113 and 0.090, respectively). The overall mean flux from the alfalfa field was almost twofold of that from the corn field (Table 3.1), however, the difference between individual fluxes from corn and alfalfa was not statistically significant (P=0.055). The corn data were more variable than alfalfa, both spatially and temporally (Table 3.1). Overall chamber fluxes showed a continuous decrease for the period over four days of observations both on alfalfa and corn sites, which was likely related to the weather and soil conditions.

Table 3.1. Descriptive statistics of N_2O flux EC and chamber measurements: mean, standard deviation, median, 10th and 90th percentiles, min, max and coefficient of variations (CV%)

Measurements	**N_2O-N flux, µg m^{-2} min^{-1}**							**Daily CV%, mean**
	Mean	**STD**	**Median**	**10%-ile**	**90%-ile**	**Min**	**Max**	
Eddy covariance (half-hour fluxes)	2.3 (n=75)	7.4	1.1	-3.4	10.2	-10.5	40.0	289[a]
Chambers in alfalfa (daily fluxes)	1.1 (n=74)	1.2	1.0	-0.1	2.5	-1.1	5.6	132[a] 123[b]
Chambers in corn (daily fluxes)	0.6 (n=74)	1.5	0.3	-0.8	2.8	-2.4	6.1	161[a] 188[b]

[a] - temporal variability
[b] - spatial variability

Comparison between the eddy covariance and chamber results showed that EC daily means on June 30 and July 1 were similar to and on July 2 greater than alfalfa chamber fluxes. As compared to the corn chamber fluxes, EC daily fluxes were greater on June 30 –July 2. Both EC and chamber means were close to zero on July 3 (Figure 3.3). The four-day mean EC flux was approximately four times greater than corn and two times greater than alfalfa overall chamber means (Table 3.1). However daily chamber fluxes along the transect between the two fields were not significantly different from the daily mean EC flux (P=0.486 and 0.118 for alfalfa and corn, respectively), possibly due to the high variability of the data.

3.3.2 Soil and weather parameters

The analysis of soil mineral N prior to the beginning of the chamber campaign showed that concentrations of soil ammonium and nitrite/nitrate were substantially greater for alfalfa (22.8kg NH_4-N ha^{-1} and 53.8kg NO_3/NO_2-N ha^{-1}, respectively) than for corn (5.4kg NH_4-N ha^{-1} and 17.1kg NO_3/NO_2-N ha^{-1}), likely resulting from the greater manure loading which alfalfa field received earlier that season (Molodovskaya et al., 2009). Noticeably, soil NH_4-N levels were 1/3 to 1/2 of NO_3/NO_2-N levels for both fields.

The campaign period was characterized by dry warm weather with the exception of a strong rainstorm on the afternoon of July 3 (Figure 3.4a). The soil moisture content was steadily decreasing from 61% to 56% WFPS before that precipitation event. Daily air temperature varied within 17 to19^{o}C, close to the 30 year monthly normal for the area. The hourly minimum of 7.3^{o}C was observed during the night of July 2 resulting in the lowest of all daily means (17.2^{o}C). Soils were generally warmer than air, and the soil temperature drop on July 2 was less extreme than for the air, with the hourly

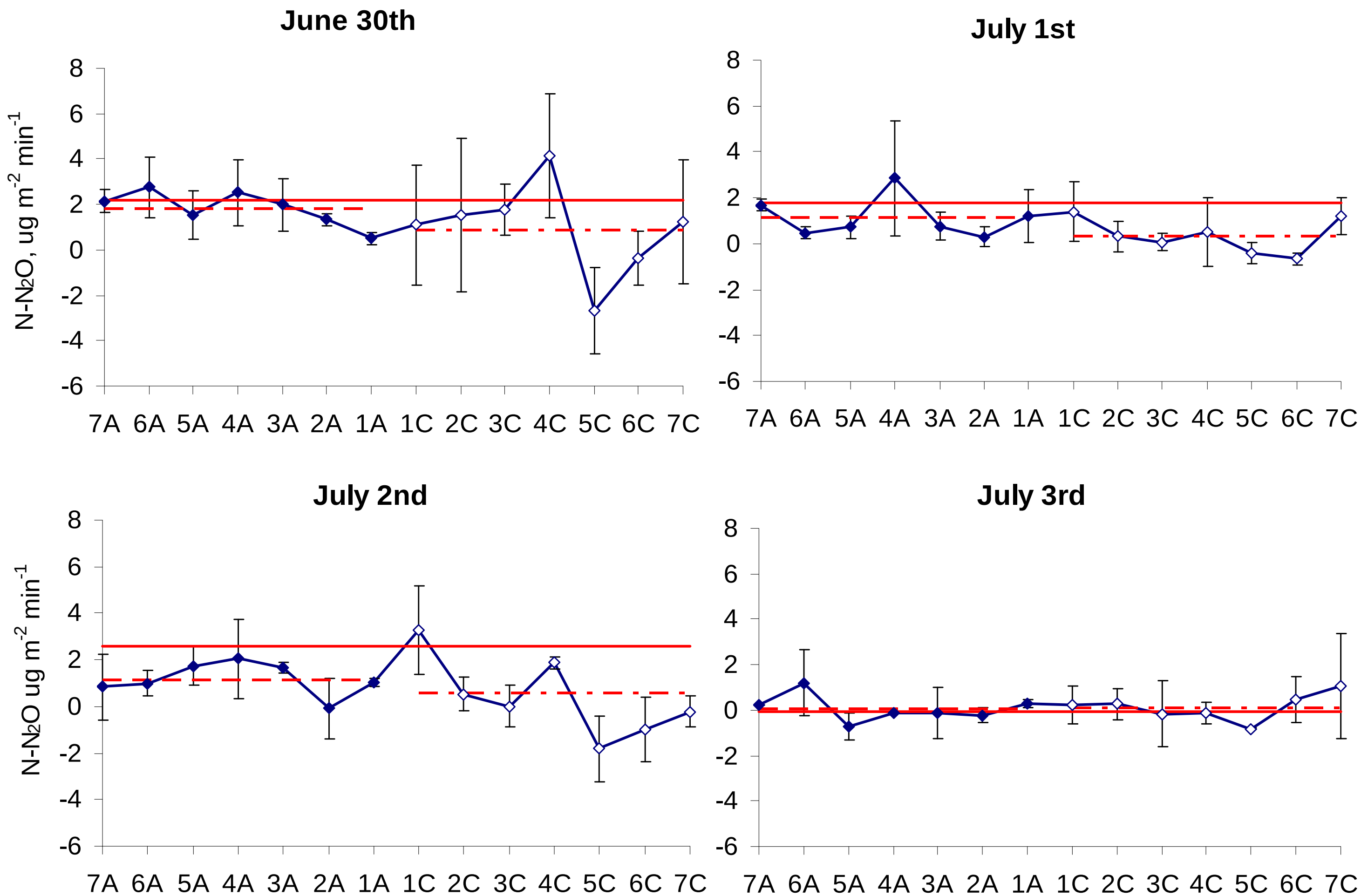

Figure 3.3. Daily N_2O-N fluxes from chambers along the alfalfa/corn field transect: 1A-7A alfalfa (♦), 1C-7C corn (◊). Straight lines depict the daily means of all alfalfa chambers (red dashed), all corn chambers (red dash-dotted), and field-scale eddy covariance (solid red) fluxes.

minimum of 13.5°C (Figure 3.4b). The dependency of N_2O-N chamber emissions on soil temperature and moisture data was not straightforward (Figure 3.5), however, the N_2O-N flux was the greatest at soil moisture ≥60% WFPS and decreased when soil moisture declined. The changes in soil temperature likely were not dramatic enough to have a strong impact on flux formation. Generally, July 2 was the driest and the coolest of all campaign days, which likely promoted a drop in N_2O flux, although the response was not immediate and did not occur until the next day as shown by both chamber and EC measurements (Figure 3.6).

3.3.3 Wind direction

During the campaign, prevalent winds were from the west, west-south-west, north-west and west-north-west (Figure 3.7a-d). The chamber-covered area was thus represented in the micrometeorological footprint of the EC measurements for the most of the time, as chambers were located south-west to north-west from the mast. The greatest N_2O eddy fluxes were observed on July 2 when winds were coming from a range of directions between west and north-west (Figure 3.7c) and presumably corn-covered fetch. However, neither corn nor alfalfa chamber data showed any increase in N_2O flux on that day, indicating the possibility of the input from sources beyond monitored fields. For the rest of observation time, June 30, July 1 and 3, wind resultant vectors varied slightly between azimuth angles of 244° and 280° and were mostly associated with the alfalfa field (Figure 3.1). No sources in this direction were within the fetch other than studied croplands, and predictably the EC and chamber measurements gave comparable results.

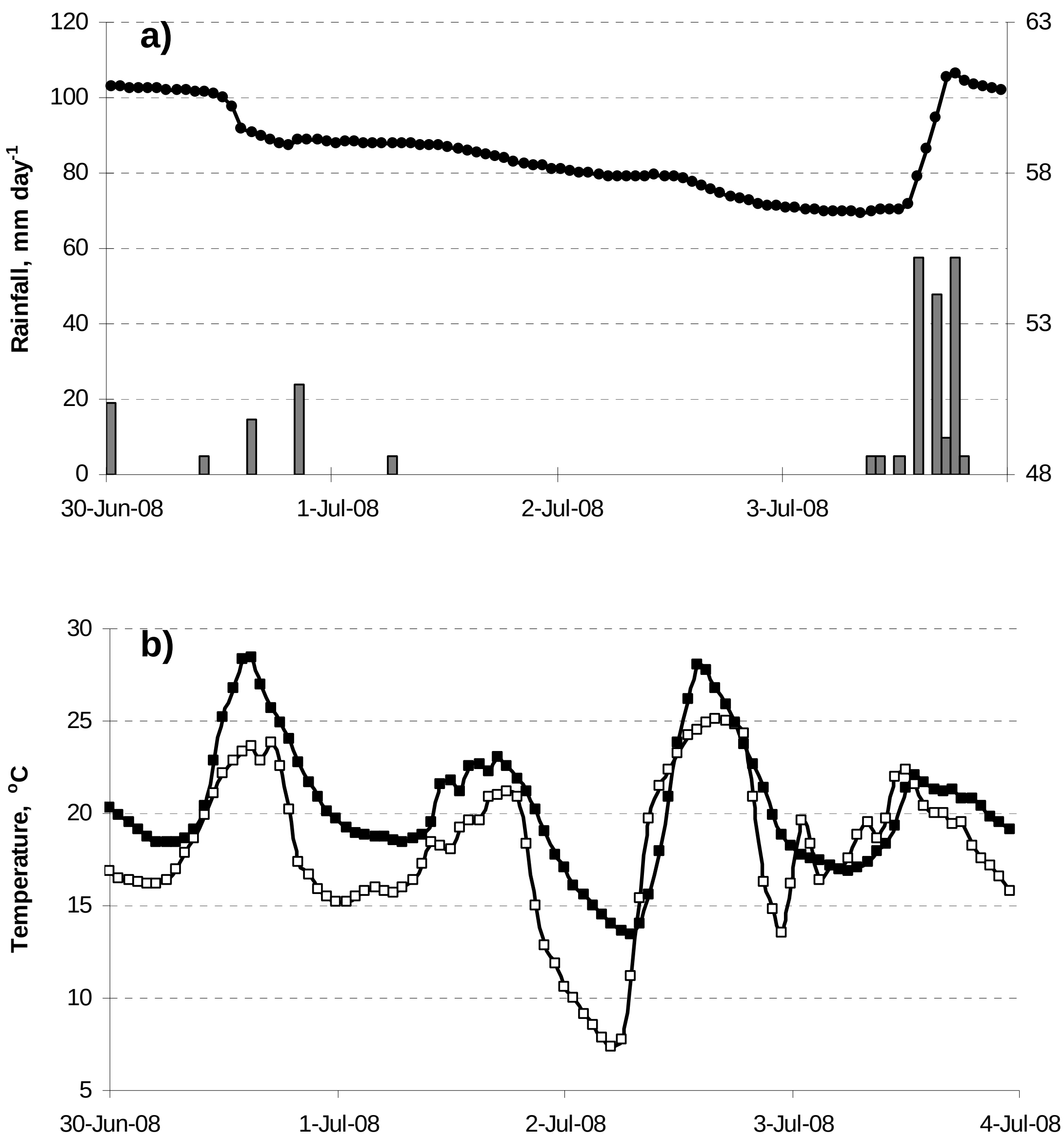

Figure 3.4. Hourly weather data at T&R Center research site: a) soil moisture content (●) and rainfall (bars); b) soil temperature (■) and air temperature (□)

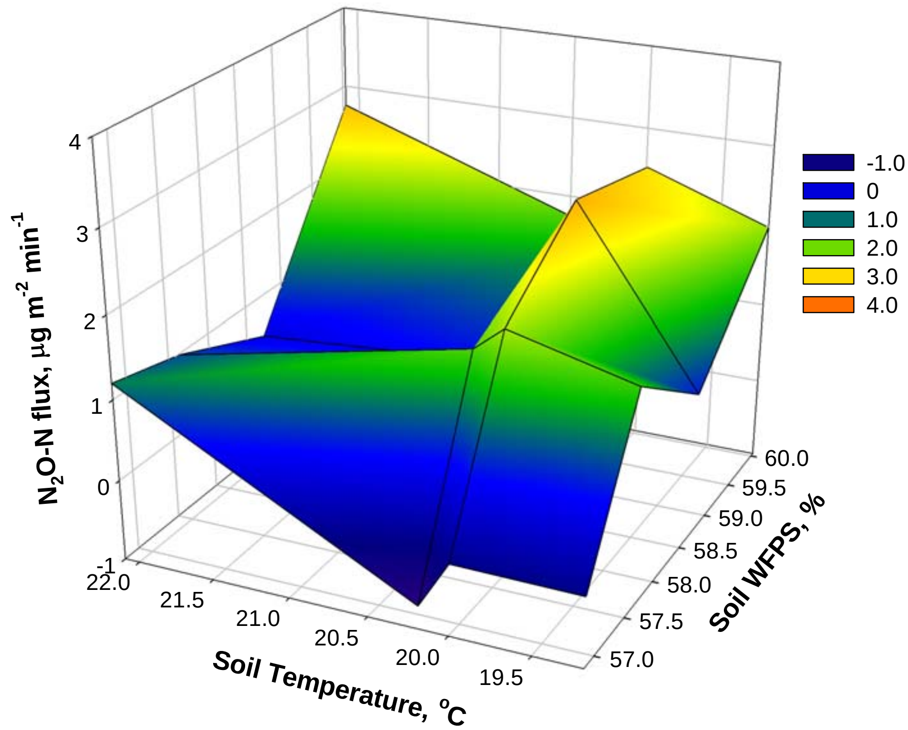

Figure 3.5. Dependency of N_2O-N chamber flux on soil temperature and moisture content

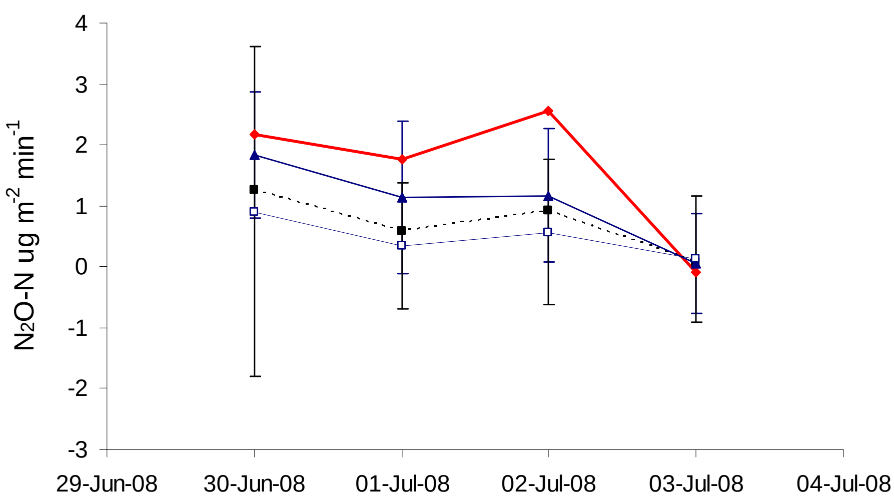

Figure 3.6. Four-day dynamics of daily chamber alfalfa (▲), corn (□) corn/alfalfa average (■) and eddy covariance (♦) N_2O fluxes

3.3.4 Negative N_2O fluxes

Approximately 28% of observed chamber fluxes (7% from alfalfa and 21% from corn) fields were negative. Although calculated daily means were above zero for the majority of chambers, certain chambers produced stable negative fluxes throughout the campaign period. In particular, chambers 5 and 6 located on the corn field (Figure 3.3) constantly had negative N_2O fluxes for days 1-4 and 1-3 of the experiment, respectively. The negative daily means varied between -0.11 and -2.66μg N_2O-N m^{-2} min^{-1}. Correction for values not significantly different from zero eliminated one third of the negative chamber fluxes. The remaining negative values were well above the flux detection limit, and likely indicated a net sink activity for N_2O in soils. For the EC half-hour N_2O fluxes, negative values above the flux detection limit constituted 35% of total emissions. Although most of them were highly scattered during the day, some were clustered for several half-hour periods, showing a consistent trend of negative emissions (Figure 3.2).

3.4 Discussion

Irregularity of N_2O formation in soils makes it difficult to compare data sets obtained by differing techniques. A large share of emissions may come from so-called persistent "hot spots", soil sites with greater denitrification activity attributed to greater organic C content (Parkin, 1987) or/and local topography promoting soil water abundance, e.g. low elevation and footslopes (Corre et al., 1996; Yanai et al., 2003). Since individual chambers cover only a small part of the soil surface, they are especially sensitive to soil N_2O anisotropy, and chamber datasets often show high spatial variability with coefficients of variation greater than 100% (Ambus et.al, 1994; Clayton et al., 1994; Pihlatie et al., 2005; Flechard et al., 2007). Temporal N_2O variability could be similarly high; it is mostly related to the seasonal changes in soil

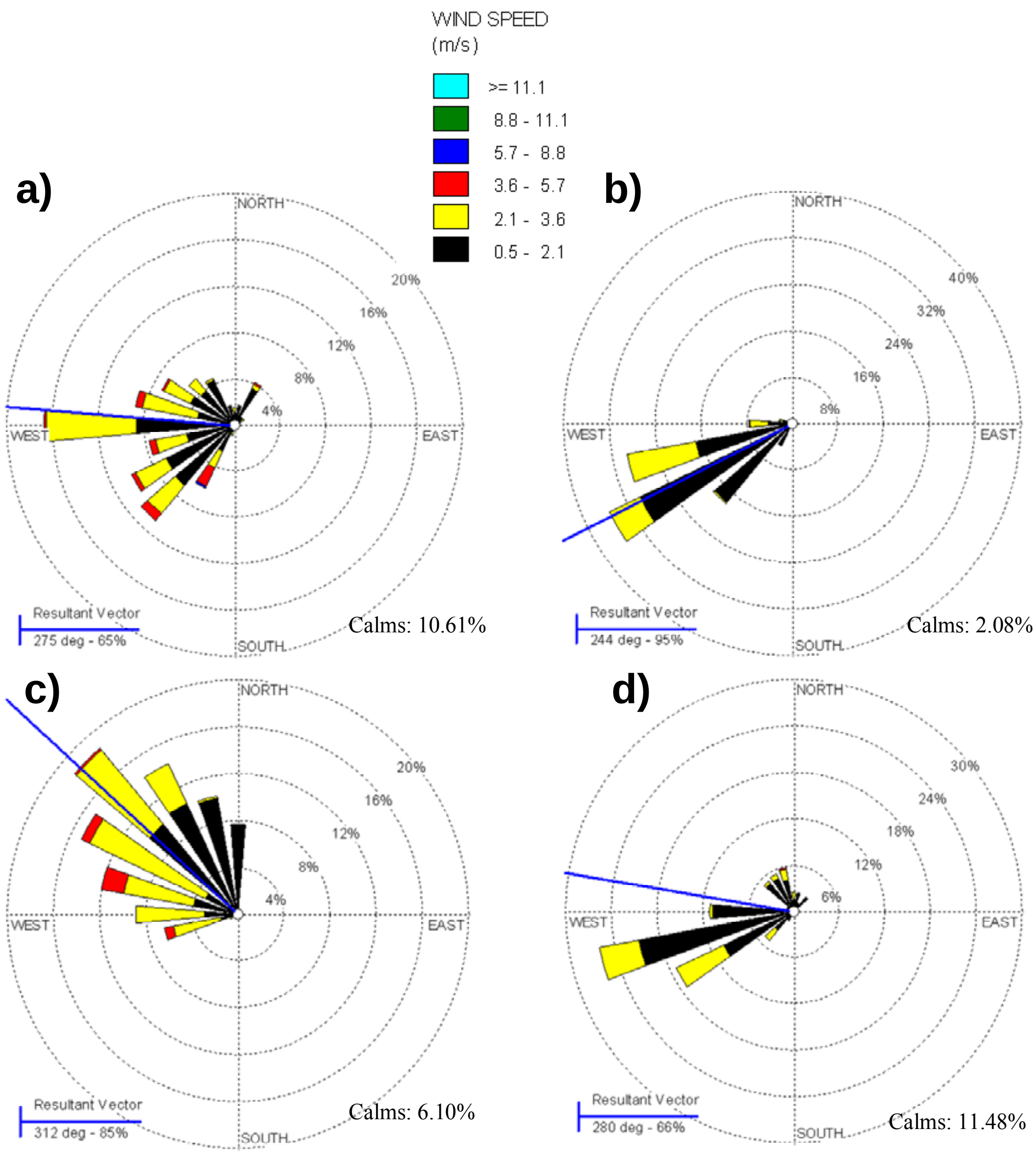

Figure 3.7. Wind roses from T&R Center research site on (a) June 30, (b) July 1, (c) July 2 and (d) July 3, 2008.

N and climate parameters, such as temperature and soil moisture (Laville et al., 1999) and thus harder to monitor with chambers due to their low sampling frequency. The high-frequency eddy covariance technique much better represents temporal flux variability; however, large variation still can be observed due to instrumental and statistical uncertainties from single-point measurements and short averaging periods (Pihlatie et al., 2005).

Our simultaneous measurements of N_2O by EC and chambers on alfalfa and corn fields for four summer days gave comparable flux estimates. In the absence of extreme weather events, the variation in chamber fluxes from both alfalfa and corn was within a narrow range from -1.1 to +5.6μg N_2O-N m^{-2} min^{-1} for alfalfa and from -2.4 to +6.1μg N_2O-N m^{-2} min^{-1} for corn, with ~25% of total fluxes below the minimum detection limits. The variability of half-hour EC data was much greater, with emission ranging between -10 and +40μg N_2O-N m^{-2} min^{-1}. Similar differences in variability ranges for EC vs. chamber measurements were reported by Pihlatie et al. (2005) and Neftel et al. (2007) for forested and grass-covered areas, respectively, with both representing mostly background fluxes. In their study of CO_2 fluxes, Reth et al. (2005) also found that chamber fluxes showed more or less smooth daily cycles and did not follow the scattered peaks of EC measurements.

Although daily mean EC fluxes were generally greater than chamber fluxes, the difference between the two methodologies was still within the range of uncertainty, probably due to the high variation of the EC data (Table 1), similar to the results of Christensen et al. (1996). No flux events were triggered by the abrupt weather changes during the campaign period, but the continuous drop in soil moisture and temperature over the four observation days could possibly explain the decrease in both chamber and EC fluxes on July 3 (Figure 3.6).

The wind direction and footprint analysis showed that approximately 75% of the integrated daily EC flux was primarily constituted by emissions from within 150 m west to west-south-west from the mast, i.e. area under alfalfa treatment, which was confirmed by the very similar daily EC and alfalfa chamber means. When winds were blowing from a much wider range of directions from west to north (July 2), the EC data showed both very scattered fluxes and a greater daily mean, which was not associated with either field treatment (Figure 3.2). It was however hard to distinguish if the increase reflected real emission levels or resulted from instrumental uncertainty, as the daily mean value was still within STD range. Sources beyond the chamber monitored areas could contribute to the EC flux, for example, the small sporadically-grazed grass plot located on the edge of footprint to the north-west from the mast. Another possibility is that rapid changes in wind direction could cause non-stationarity in N_2O signal, as described by Laville et al. (1999). The location and amount of chambers are thus critical for the proper estimate of variability of the integrated flux both on the temporal and spatial scale.

Net N_2O uptake by soils resulting in the negative fluxes also contributed to the high variation of emission data. Negative N_2O fluxes are often documented for the closed-cycle ecosystems with low soil N, such as forests and non-fertilized grasslands (Rosenkranz et al., 2006; Neftel et al., 2007). In many cases, researchers only mention negative values as random uncertainties or instrumental noise, since N_2O fluxes are often measured at the levels very close to method detection limits (Skiba et al, 1996; Merino et al., 2004), and soils were long not considered as a serious sink for N_2O.

However, some cases of N_2O uptake have been reported for fertilized ecosystems, e.g. Glatzel and Stahr (2001) reported net N_2O consumption up to -41.2μg N_2O-N m^{-2} hr^{-1} for fertilized grasslands and Li et al. (2008) observed mean negative N_2O fluxes of -0.75mg N_2O m^{-2} hr^{-1} for four days in fertilized maize field. Chapius-Lardy et al. (2007) reviewed more than 150 scientific reports on N_2O net uptake and found that in many cases negative N_2O fluxes were well beyond uncertainty ranges and could not be treated simply as instrumental errors.

In our study, the N_2O uptake was observed more often on the corn site, which received six times less manure N fertilization in 2008 than the alfalfa field. A few chambers continuously monitored negative fluxes above the method detection limit throughout the period of observation (Figure 3.3), which was not a field-scale trend, but rather an indication of consistent microsites, similar to denitrification "hot spots". However, the mechanisms of N_2O soil uptake are not well understood. The most common theory explaining N_2O net uptake is that in the absence of other forms of oxidized N in soils, the microbial denitrifiers consume soil-formed N_2O as an electron acceptor, thus reducing N_2O to N_2 gas and completing the final step of denitrification (Neftel et al., 2007; Chapius-Lardy et al., 2007). In this case, N_2O uptake will dominate N_2O production and much of the N_2O generated in the soil column is consumed before reaching the soil surface. The process of net N_2O uptake is therefore expected to be favored by high soil moisture content (>80% WFPS) and low soil N.

The impact of environmental parameters on N_2O reduction is not always straightforward. In our case, soil N_2O consumption was observed in relatively well aerated soils and dry conditions, similarly to Rozenkranz et al. (2006) and Khalil et al. (2002). The N_2O uptake under low soil moisture (<60% WFPS) could be explained by the existence of anaerobic microsites, such as soil aggregates, in otherwise well-aerated soils. Neftel et al. (2007) mentioned that due to the low water solubility of O_2, anaerobic environments can also be created under thin water membranes, and denitrification can proceed on surfaces covered by films of less than 200μm. The anaerobic aggregates and thin water films are likely to form in moldboard-plowed, gravel-rich soils of our research sites possibly promoting N_2O uptake. This assumption however, needs further verification both on the field-scale and column-scale levels.

The combination of the field-scale eddy covariance and local-scale static chamber N_2O measurements can be a useful tool for the estimates of N_2O flux variability. The EC technique can be continuously run over extended periods of time providing information on the temporal variability in N_2O emissions, thus compensating for chamber's low frequency and gaps in data. Chambers, however, give useful insight into spatial distribution of N_2O flux formation and local emission sources and sinks, which are difficult to study by the footprint-integrated micrometeorological approach. Two methods therefore can be complementary to each other, rather than substitutive, and if run simultaneously, for instance, during short-term field campaigns, may help improve N_2O emission data quality.

3.5 Conclusions

The comparison between eddy covariance and static chamber measurements of N_2O emissions from agricultural croplands demonstrated that average daily fluxes were in good agreement, although high variability of the emissions largely contributed to uncertainty between the two data sets. The variability of chamber measurements was mainly caused by high spatial heterogeneity of soil N_2O formation, which resulted in both net N_2O production and consumption. The EC measurements however reflected integrated N_2O fluxes which were averaged over the footprint area and showed net N_2O release. The simultaneous integrated eddy covariance and chamber measurements could be a useful tool for cross-validation of different scale methods and improving the data quality on spatial and temporal variability of N_2O emission, especially when integrated flux is measured over non-uniform landscapes.

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CHAPTER 4

TEMPORAL VARIABILITY OF NITROUS OXIDE FLUXES FROM FERTILIZED CROPLANDS: ANNUAL DISTRIBUTION OF PEAK EMISSION EVENTS

4.1 Introduction

Adverse effects of agricultural nitrous oxide (N_2O) as a greenhouse gas and stratospheric ozone destructor has been a concern of environmental science and policy for over a decade (IPCC, 1996; Mosier et al., 1998; Kroeze et al., 1999; Bouwman and Boumans, 2001; Crutzen et al., 2008); however, there are still uncertainties in quantification of N_2O emissions, related foremost to the large spatial and temporal variability of N_2O formation in agricultural soils. Soil N_2O is produced through a number of microbiological and chemical processes, most importantly, autotrophic nitrification and heterotrophic denitrification (Anderson et al., 1993; Bremner, 1997; Barnard et al., 2005). N_2O from nitrification is a byproduct of ammonium (NH_4^+) oxidation to nitrites (NO_2^-) and nitrates (NO_3^-). N_2O from denitrification is an intermediate product of NO_3^- and NO_2^- reduction to di-nitrogen (N_2) gas, with the net upward flux resulting from the balance between N_2O production and consumption.

Soils, therefore, can act as a source and sink for N_2O. The strength of soil N_2O sources is determined by the availability of mineral N, microbiological activity and transport mechanisms. The latter two depend heavily on soil aeration and O_2 content, which, in turn, are controlled by the soil moisture content. Many researchers found peak N_2O formation at the soil moisture within 50-90% water-filled pore space range, when soil oxygen levels favor incomplete denitrification of NO_2^-/NO_3^- to N_2O (Smith et al., 1998; Choudhary et al., 2002; Sehy et al., 2003; Smith et al., 2003; Flechard et al., 2007). Manure fertilization provides ammonium available for nitrification, in which case a significant portion of N_2O can also be produced at 35–60% WFPS (Bateman and Baggs, 2005). A strong dependency of N_2O emissions on soil moisture status largely determines its event-induced nature, with the greatest flux peaks often resulting from abrupt changes in soil moisture status such as strong rainfall events. Temperature is another important factor for N_2O formation, with N_2O emission rates both from nitrification and denitrification increasing with soil temperature. Linear or exponential relationships between temperature and N_2O flux are well documented (Goodroad and Keeney, 1984; Smith et al., 1998; Smith et al., 2003). When soil mineral N is not limiting, concurrent rapid increases in soil temperature and soil moisture enhance denitrification, such as during spring thaw, commonly reported for temperate climate zones as promoting N_2O emissions (Goodroad et al., 1984; Wagner-Riddle and Thurtell, 1998; Izzauralde et al., 2004; Regina et al., 2004; Dusenbury et al., 2008; Matzner and Borken, 2008).

Numerous interplays between climatic factors and ecosystem-specific characteristics, e.g. soil properties, land treatment and topography, result in highly variable, sporadic nature of the N_2O net flux. In addition to spatial variability resulting from soil anisotropy, agricultural N_2O fluxes are also characterized by strong temporal fluctuations. Available N_2O data often show that while N_2O fluxes are typically at background levels or close to zero, abrupt N_2O spikes caused by the seasonal environmental or anthropogenic changes can be orders of magnitudes greater than the background emissions (Jacinthe and Dick, 1997). Parkin and Kaspar (2006) observed strong peak events which accounted for 45-49% of the cumulative annual N_2O flux from corn fields monitored for two consecutive years. In three months of continuous N_2O measurements on a dairy farm on peat land in the Netherlands, 40% of total N_2O

emission was due to a single fertilization event (Kroon et al. 2007). Scanlon and Kiely (2003) documented three major emission events, covering a timeframe of 16 days (6.6% of the total eight-month measurement period) and contributing 51% of the cumulative N_2O flux; two of those events occurred during the summer and the third occurred during the winter, however, all of them followed fertilization combined with the strong rainfall. In general, peak events of N_2O flux observed in response to precipitation, fertilization, and spring freeze/thaw cycles are believed to be the major contributors to overall annual emissions.

The episodic nature of N_2O flux makes it challenging to estimate cumulative emissions experimentally. Most current N_2O databases were obtained with static closed chambers, chosen for their low cost and operational simplicity. Chambers are helpful for small-scale measurements and monitoring spatial distribution estimates of fluxes (e.g. Yates et al., 2006; Singurindy et al. 2009). However, their low sampling frequency (semi-weekly to semi-monthly in most long-term studies) can result in emission events being either missing or over-represented in total estimates, which makes the method less suitable for studying N_2O temporal variability (Parkin, 2008). Ranging emission levels from "background" to "high peaks" and proper interpretation of N_2O flux intensity can therefore help in misrepresentations in annual emission estimates. The availability of high-frequency N_2O monitoring is essential for such an investigation.

Recently, micrometeorological methods such as eddy covariance have become more popular for the routine N_2O flux measurements. Designed for continuous observations, they can be a reliable tool for estimating temporal patterns of soil N_2O release, especially since the experimental system, once installed, can be field-operated on an annual basis without requiring much additional labor and/or technical resources.

In this study, manure-fertilized crop fields of a large dairy farm in the New York State were continuously monitored for N_2O emissions during 2006-2009 with micrometeorological eddy covariance technique. The effect of manure N fertilization on annual N_2O emissions based on the monitoring observations was discussed elsewhere by Molodovskaya et al. (2009a). This paper focuses on the analysis of temporal variability of the three and half year dataset of daily N_2O fluxes: how the environmental factors such as soil moisture and temperature affected the temporal distribution of the N_2O flux throughout the year; what triggered N_2O high peaks, and how they contributed to total annual emissions.

4.2 Materials and methods

4.2.1 Research site

Eddy covariance monitoring of agricultural N_2O fluxes was conducted at the manure-fertilized fields of the large-size dairy farm (Cornell University Animal Science Teaching and Research Center) located in Harford, New York State, USA. The area has a humid continental climate with annual 30-year average temperature 7.8^oC, rainfall 932mm and snowfall 175cm. The length of the freeze-free season varies from 120 to 150 days.

Fields under alfalfa and corn were continuously monitored for N_2O emissions and weather parameters from April 2006 to May 2009. Alfalfa field was the experimental site during growing season (April-October) in 2006; the system moved to a different field in 2007, initially under corn, where it stayed thereafter. In 2008, approximately half of the field area was rotated to alfalfa whereas the remainder stayed in corn. All fields were fertilized with liquid and/or semi-solid manure broadcasted without immediate incorporation. The alfalfa field received ~300kg total manure N ha^{-1} with mostly liquid manure in summer/early fall of 2006, immediately following the harvest. The corn field was fertilized in winter/early spring of 2007 on the top of snow cover and the amount of total manure N was 1300kg N ha^{-1}. The alfalfa portion of the split alfalfa/corn site was fertilized with 750kg total manure N ha^{-1} in winter/spring of 2008; the corn portion of the same site received 125kg total manure N ha^{-1} in May 2008. No manure was applied to the fields in winter or spring of 2009. Site characteristics, soil properties, and manure and nitrogen loads were described in detail elsewhere (Molodovskaya et al., 2009a).

4.2.2 Eddy covariance system

The eddy flux of N_2O was calculated as a product of instantaneous changes in vertical wind velocity and N_2O gas concentration (Pattey et al., 2006), which were measured by 3-D sonic anemometer (model CSAT3; Campbell Scientific, Inc.) and a TGA100A Tunable Diode Laser Absorption Spectrometry/Trace Gas Analyzer (TDLAS/TGA; Campbell Scientific, Inc.), respectively.

The sonic anemometer and sampling inlet for TDLAS/TGA were mounted in close proximity on the same mast (3.5m high). The mast was situated next to the driveway between the fields which also served as dividing line between alfalfa and corn sites starting 2008. Measurements were taken at 10Hz and integrated over 30min intervals. The flux lowest detection limits were calculated for each year using Pihlatie et al. (2005) formula from the signal noise of concentration measurements and standard deviation of the vertical wind speed; for the half-hour averaging periods the detection limits were 0.015; 0.016; 0.013 and 0.015μg m^{-2} s^{-1} in 2006, 2007, 2008 and 2009, respectively. The data filtering was performed for all high-frequency data, and the details of quality control procedure are given by Molodovskaya et al. (2009a,b). The data filtering resulted in 51% of good quality data in 2006, 72% in 2007, 69% in 2008 and 70% in January-May of 2009. Quality assured half-hour fluxes were averaged over daily periods.

4.2.3 Soil and weather parameters

In addition to the parameters for eddy covariance calculation, a number of soil and weather characteristics were also measured at the same time including air temperature and humidity (HMP45A/D probes; Vaisala Group) and precipitation (tipping bucket rain gauge). High-frequency monitoring of volumetric soil moisture content (replicate CS616 water content reflectometers, Campbell Scientific, Inc.) and soil temperature (four replicate thermocouple probes) at depths of 10cm were added to the system in December 2006 and July 2007, respectively. The CS616 reflectometer was field-calibrated by the standard soil-core gravimetric method and calibration coefficient was determined from a curve fit of known water content and sensor output. In 2006, before soil moisture sensors were installed in soils on a permanent basis, soil moisture was determined from gravimetric moisture content and bulk density measured bimonthly by the soil core method.

Soil samples were collected bimonthly from May to September in 2006 and monthly from April to December in 2007 – 2008 on each site from the surface 10cm of soil using a 5-cm diameter aluminum soil core. The samples were refrigerated at 4°C before analysis. For gravimetric moisture content and bulk density determination, samples were oven-dried at 105°C for 24 hrs. The NO_2/NO_3-N contents were analyzed after extraction with 2*M* KCL. For extract preparation, 5g of the field-moist soil was placed in centrifuge tubes with 50mL of 2*M* KCl, stoppered, shaken for 30min, centrifuged at 3000rpm for 40min and filtered through 0.45μm membrane filters (Pall Life Science Corp., East Hills, NY). The supernatant was analyzed for NO_2/NO_3-N colorimetrically by sulfanilamide method with continuous flow spectrophotometer (Astoria Analyzer; Astoria Pacific, Inc.)

4.2.4 Data analysis and statistics

Data time series were analyzed for autocorrelation and cross-correlation between N_2O flux, air/soil temperature and soil moisture data. The power spectra of the time series (the amplitudes of multiple cosine waves of varying wavelengths added to each other to reconstruct the observed time series) were determined over the 512 day interval from April 1, 2007 to December 31, 2008 (days with no or minimum data gaps) and analyzed for seasonal periodicity of N_2O flux events. Flux calculations, quality control and time series analysis were carried out using Matlab, version 7.0 (The MathWorks, Inc.).

4.3 Results

4.3.1 Air and soil temperatures

In 2006-2009, daily air temperatures varied from the minimum of -19^{o}C in mid-January 2009 to the maximum of 28^{o}C in June 2008 (Figure 4.1a). The average growing season (April-October) air temperatures were 17, 14 and 14^{o}C for 2006, 2007 and 2008, respectively (as compared to the 30-year growing season mean of 15^{o}C). The warmest months were July in 2006 and 2008 (22^{o}C and 20^{o}C, respectively), and August in 2007 (19^{o}C) (the 30-year normals for July and August

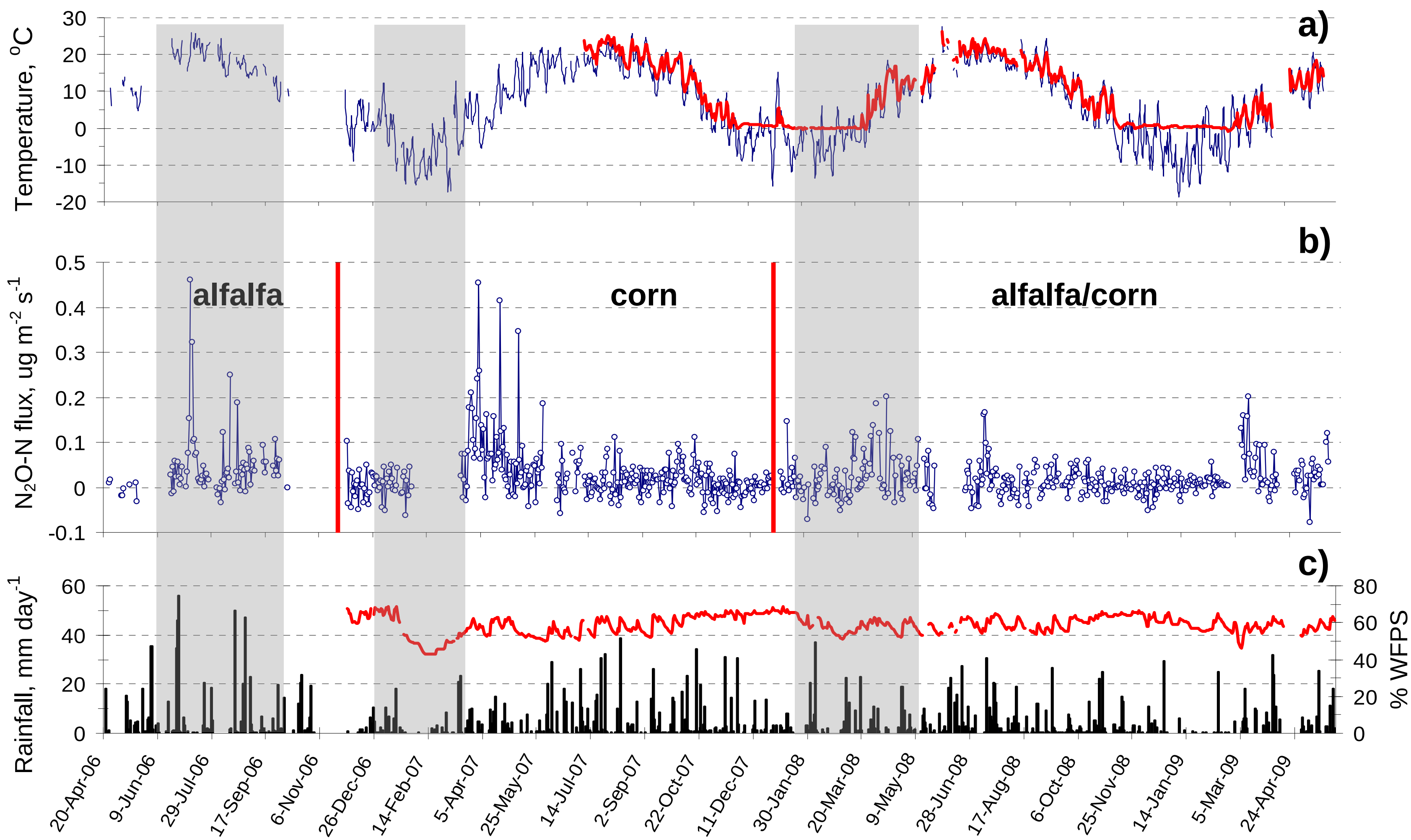

Figure 4.1. Daily mean (a) air temperature (blue line) and soil temperature (red line), (b) nitrous oxide fluxes and (c) rainfall (bars) and soil moisture content (red line) at Harford T&R Center. Grey-shaded areas indicate periods of manure application

20 and 19^oC). The non-growing season (November- March) averages were around 0^oC for 2007-2008 and 2008-2009, respectively (the 30-year non-growing season normal 1^oC). The coldest months were February in 2007 and 2008 (-8 and -5^oC; the 30-year normal -4^oC) and January in 2009 (-9^oC; the 30-year normal -5^oC).

Abrupt temperature fluctuations were observed mostly on early spring in 2007, 2008, and 2009. The most prominent temperature changes occurred in March-April 2007: March 6-14 (when air temperature increased by 30^oC within 1 week), March 17-27 (17^oC rise) and April 7-23 (22^oC rise). The 2008 and 2009 spring temperatures rose more gradually, with the exception of abnormally large fluctuation with magnitude of 31^oC in 3-8 January 2008 (Figure 4.1a).

Soil temperature measurements (starting midsummer 2007) generally followed air temperature cycles at >0^oC in the warmer months. In winter, however, soil temperatures at the depth of 10cm often remained above or around 0^oC even when associated air temperatures dropped largely below freezing. Spring thaw typically occurred in March to early April, and soil freeze/thaw cycles were more pronounced in spring 2009 (Figure 4.2a, b).

4.3.2 Precipitation and soil moisture conditions

Along with the warmest temperatures, the growing season of 2006 was also characterized by the greatest rainfall (Figure 4.1c), with 700mm observed from April to October. By comparison, growing season rainfall was 481mm (895mm annual) in 2007 and 438mm (833mm annual) in 2008, as compared to 30-year mean values of 454mm for the growing season and 930mm annual. The peak rainfall months were June and July for each year. Heavy rainfall in summer 2006 resulted in the greatest

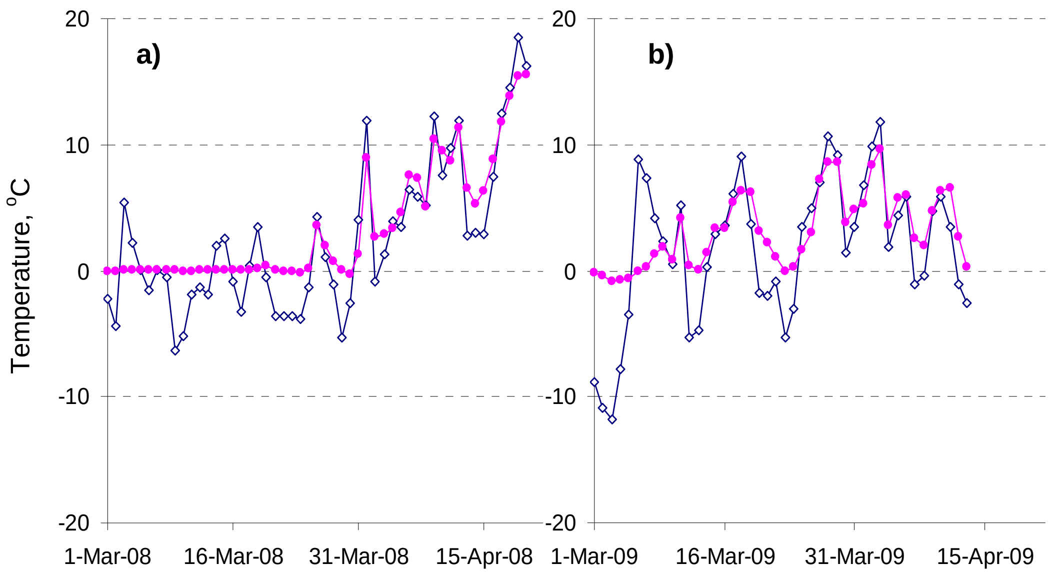

Figure 4.2. Soil freeze/thaw cycles in 2008 (a) and 2009 (b). Soil temperature (•) was measured at 0.1 m below ground, air temperature (○) was measured at 3 m above ground

soil moisture content for all seasons that reached its peak of 91% of water-filled pore space (WFPS) in July (not shown on the graph). As Figure 4.1c shows, soil water contents for 2007 -2009 primarily varied within the relatively narrow range of 50% to 68% WFPS. Rises in soil moisture content usually followed strong precipitation events during growing season months. Soil moisture conditions were more stable from November to January, with the greatest annual peak values (65-68%) for each year. Decreases attributed to the winter freezing were observed in February (45% lowest) of each year; and gradual rises up to 60% related to the spring soil thaw were observed in March and April.

4.3.3 Manure and soil mineral nitrogen

The greatest soil nitrate and nitrite concentrations generally followed manure fertilization events (Table 4.1) and were observed in July 2006 and April-May 2007 and 2008. The annual pattern of soil NO_2/NO_3-N showed gradual decrease by the end of growing season related foremost to the crop N uptake and a later small rise in October – November after the crop harvest. As expected, the greatest manure application rates in 2007 led to the greatest values of NO_2/NO_3-N concentrations in soils. The lowest NO_2/NO_3-N was observed for the corn part of the monitored field in 2008, which received the least of all manure loadings.

Table 4.1. Mean monthly soil nitrate/nitrite contents (standard deviation in parentheses) and monthly manure N loadings.

	2006 (alfalfa)		**2007 (corn)**		**2008 (split alfalfa/corn)**	
	NO_2/NO_3-N, kg ha^{-1}	**Manure N applied, kg ha-1**	**NO_2/NO_3-N, kg ha^{-1}**	**Manure N applied, kg ha-1**	**NO_2/NO_3-N, kg ha^{-1}**	**Manure N applied, kg ha-1**
January	-	-	-	634	-	185[a]
February	-	-	-	340	-	181[a]
March	-	-	-	246	-	500[a]
April	-	-	115(27)	-	66(27)[a] 24(6)[b]	252[a]
May	11(3)	-	105(46)	-	67(28)[a] 29(16)[b]	121[b]
June	-	63	63(27)	-	54(7)[a] 17(5)[b]	-
July	59(30)	143	45(27)	-	40(28)[a] 5(2)[b]	-
August	-	78	39(17)	-	23(8)[a] 9(2)[b]	-
September	57(31)	7	37(14)	-	22(2)[a] 7(0)[b]	-
October	-	-	37(8)	-	33(14)[a] 13(5)[b]	-
November	-	-	40(7)	-	42(7)[a] 16(6)[b]	-
December	-	-	45(10)	-	33(5)[a] 13(6)[b]	-

[a] - Alfalfa part of the field
[b] – Corn part of the field

4.3.4 Nitrous oxide flux

The time series of daily N_2O emissions in 2006-2009 demonstrated largely scattered fluxes which were low or close to zero for most of the time but with the peak values exceeding annual and growing season means more than an order of magnitude (Figure 4.1b). Nitrous oxide fluxes from both corn and alfalfa sites were highly variable. The coefficients of variance (CV) for 2006, 2007 and 2008 daily mean values were 160%, 238% and 328%, respectively. The greatest N_2O-N peaks were observed in July for summer fertilized alfalfa field and in March-April for winter fertilized corn and split corn/alfalfa fields. Summer N_2O events were short intense peaks spiking from zero background and lasting from 1 to 10 days. Winter N_2O releases generally lasted longer - several weeks each in 2007 and 2008 - and, in contrast to summer, formed atop the elevated emission baseline. Annual and growing season means, maxima, minima and coefficients of variation are shown in Table 4.2.

Table 4.2. Descriptive statistics for the annual and growing season N_2O emissions from manure fertilized fields in New York State (incomplete 2009 data set was not included in time series analysis).

Year (crop)	**N_2O flux, µg m^{-2} s^{-1}**				**Coefficient of variation (CV), %**	**Number of observations (n)**
	Annual mean (median)	**Growing season (Apr-Oct) mean (median)**	**Min**	**Max**		
2006 (alfalfa)	-	0.045 (0.028)	-0.034	0.460	160	84
2007 (corn)	0.026(0.015)	0.029 (0.020)	-0.062	0.455	223	322
2008 (alfalfa/corn)	0.016(0.007)	0.018 (0.014)	-0.072	0.200	256	267

The analysis of power spectra of the time series April 1, 2007 to December 31, 2008 showed no apparent dominant periodicity in the N_2O signal. Fluxes below detection limits were observed for 24%, 37% and 37% of total monitoring time in 2006, 2007 and 2008, respectively, and can be considered instrumental noise. The remaining data included both negative and positive N_2O fluxes, with negative values totaling up to 14% of daily observations above the detection limit. Positive fluxes indicating net N_2O-N release to the atmosphere thus accounted for ~50% of total daily measurements in 2006-2008.

4.4 Discussion

4.4.1 "High" vs "low" N_2O fluxes

Analysis of the available datasets on N_2O emissions from fertilized corn and alfalfa/grassland showed that fluxes are often referred to as "low" or "background" when they do not exceed 0.03-0.05μg N_2O-N m^{-2} s^{-1} (Scanlon and Kiely, 2003; Sehy et al., 2003; Neftel et al., 2007; Dusenbury et al., 2008). The reported spectrum of elevated or "high" emissions is usually much broader, which reflects the high variability of N_2O fluxes and strong dependence of measurements on experimental conditions such as climate, soil properties, land treatment and fertilization. N_2O fluxes reported as "high" or "peak" generally vary within 0.08 - 0.6μg N_2O–N m^{-2} s^{-1} (units adjusted) (Goodroad et al., 1984; Wagner-Riddle and Thurtell, 1998; Laville et al., 1999; Khalil et al., 2002; Sehy et al., 2003; Rochette et al., 2004; Venterea et al., 2005; Hsieh et al., 2005; Drury et al., 2006; Flechard et al., 2007). Indeed, any categorization of N_2O emissions is relative, and in most cases only appropriate for the fluxes within the same dataset or specific measurement range.

For the purpose of this research, we divided daily N_2O fluxes measured at our sites in 2006-2009 into three categories by their absolute values: "high peaks" (>0.1μg m^{-2} s^{-1}), "medium fluxes" (<0.1 and >0.05μg m^{-2} s^{-1}) and "background" (<0.05μg m^{-2} s^{-1}). The numerical thresholds were chosen based on both previous studies of manure-fertilized corn and alfalfa and our specific range of measurements. The percentage contribution of each flux category to the annual cumulative emission and covered timeframe was calculated (Table 4.3), and simple comparison of those contributions showed that high peak events that lasted for 11% or less of total monitoring time were responsible for ~40-50% of cumulative annual emissions.

Table 4.3. Categorization of N_2O fluxes: percentage of annual emissions and of observation time.

Year / Peak value, μg m^{-2} s^{-1}	2006 (alfalfa)		2007 (corn)		2008-2009 (split alfalfa/corn)	
	% of cum N_2O emission	**% of covered time**	**% of cum N_2O emission**	**% of covered time**	**% of cum N_2O emission**	**% of covered time**
>0.1	39	4	47	7	47	11
<0.1 and >0.05	37	8	33	12	25	16
<0.05	24	88	9	81	28	73

Understanding N_2O high peak triggering factors and temporal distribution is essential for proper estimation and prediction of agricultural N_2O emissions. The effect of manure fertilization on N_2O peak events and annual emissions was previously discussed in Molodovskaya et al. (2009a). Here, we focus on the importance of environmental parameters such as temperature and soil moisture and how their interactions affect N_2O high peak generation throughout annual agricultural cycles.

4.4.2 Temperature and soil moisture effect

The amount of precipitation during the last week of June in 2006 was 40% greater than 30-year monthly normal for the area. Together with simultaneous manure spreading and a local temperature maximum observed few days later, it resulted in an extremely intense N_2O peak event that lasted for over 10 days, produced 38% of total emissions in 2006 and resulted in the greatest growing season N_2O average of all years observed. Few smaller magnitude N_2O peaks were observed later during the season, all of which also followed strong (>40mm day^{-1}) rainfall events (Figure 4.1b). Daily soil moisture data were not available at that time, however bimonthly measurements showed that water filled pore space had increased from 67% in May to 91% in July, promoting N_2O formation most likely by denitrification.

Noticeably, the 2007-2009 soil moisture contents varied within the narrow range of 50-68% WFPS (Figure 4.1c), with the only exception in early spring 2007, when it dropped to 45% WFPS in February and gradually rose back to 60% until April. In the remainder of observation time, it rarely fell below 50%, so it is likely that soil moisture was not a major limiting factor for N_2O high peak formation (unlike in 2006). In the absence of limiting soil moisture, temperature changes had greater control of elevated N_2O emissions. Starting from 2007, simultaneous daily measurements of temperature and soil moisture made it possible to analyze their combined effect on N_2O high peaks more precisely. N_2O daily fluxes $\geq 0.1 \mu g\ m^{-2}\ s^{-1}$ from 2007-2009 years of observations (for growing and non-growing seasons) were plotted on corresponding daily temperature (both air and soil) versus soil moisture graph (Figure 4.3a, b).

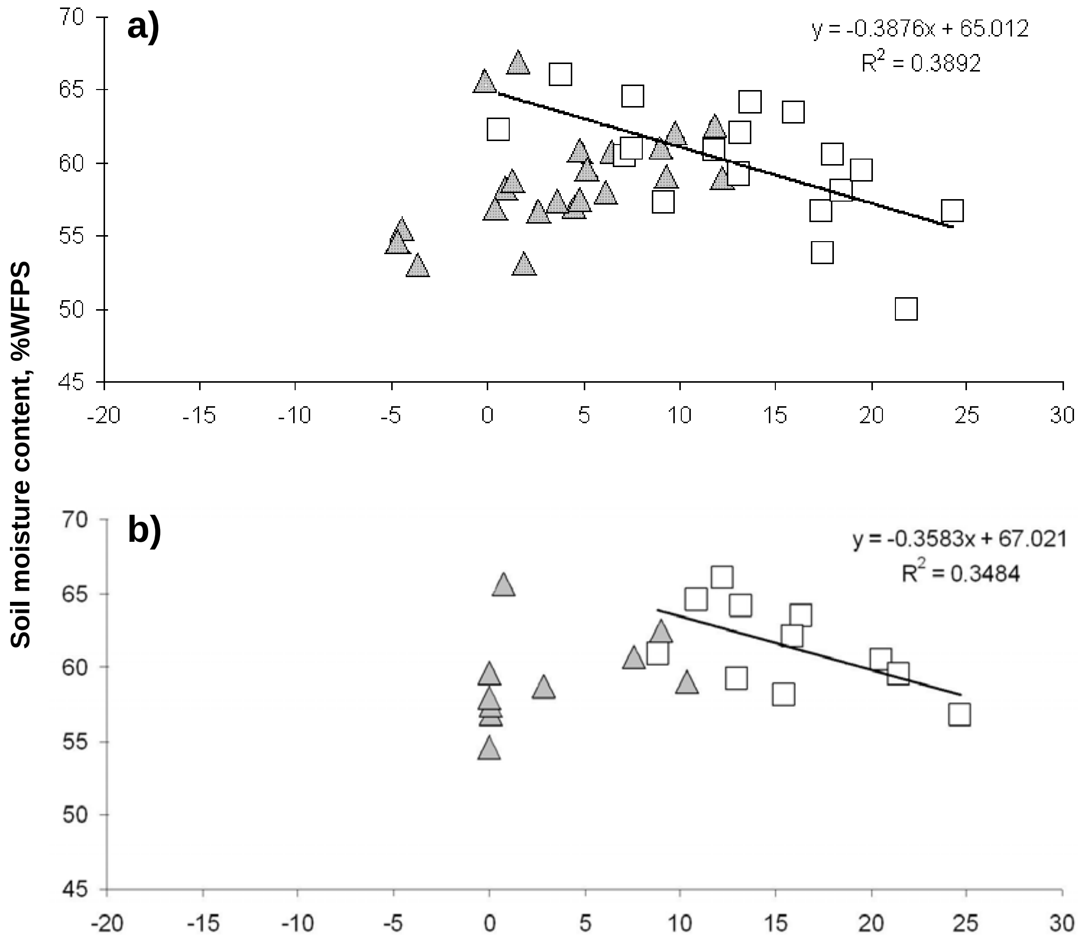

Figure 4.3. The high peak N_2O fluxes (>0.1 ug m^{-2} s^{-1}) in relation to the combined air (a) and soil (b) temperature and soil moisture conditions (all in absolute values) during growing (open squares) and non-growing including spring thaw (shaded triangles) seasons.

Relatively strong correlation was found between air and soil temperature and soil moisture for their effect on the growing season N_2O high peaks (Figure 4.3a, b). Both air and soil temperatures were inversely proportional to the soil moisture (R^2=0.39 and 0.35, respectively; $P \leq 0.05$), similar to Conen et al.(2000), indicating that within certain limits those two parameters compensate for each other with regard to N_2O formation. For the warmer April-November periods, soil and air temperature unsurprisingly followed the same cycles and were well correlated (R^2=0.91). In winter, however, soil temperatures showed greater stability in contrast to the frequent air temperature fluctuations (R^2=0.43).

The non-growing season N_2O fluxes demonstrated different response to the soil and air temperature changes. Air temperatures associated with the N_2O high peaks were highly scattered within -5°C – +15°C, whereas soil temperatures indicated that the most of non-growing season N_2O high peaks were formed at or slightly above freezing. It confirmed the importance of spring thaw for N_2O formation and was in line with Wagner-Riddle et al. (2007), who pointed out that increased N_2O fluxes are often associated with formation occurring in the warmer thawed layer above measuring probes.

The cross-correlation analysis of the yearly time series for N_2O emissions and temperature and soil moisture confirmed the lack of soil moisture effect on N_2O emissions and showed only weak correlation (correlation coefficient 0.214) between temperature and N_2O flux. Whereas the absence of a correlation between N_2O fluxes and soil moisture contents could be explained by the narrow range of soil moisture variations during the observation period, the low correlation between N_2O emissions and temperatures could be resulting from the delays in soil N_2O response to abrupt temperature changes. Delayed N_2O response to changing soil water status (between unsaturated and saturated conditions) has been reported, attributed to both slow N_2O reductase activity in first hours after transition (Firestone and Tiedje, 1979; Otte et al., 1996) and slow gas diffusion through saturated soil (Jury at al., 1982; Scanlon and Kiely, 2003). The effect of rapid temperature changes on N_2O release, to our knowledge, has not been well studied. However, in our study, simple comparison of the time of occurrence for N_2O peaks >0.1µg m^{-2} s^{-1} and temperature maxima showed that out of 17 N_2O maxima, only 10 occurred on the same day with temperature maxima; four N_2O peaks were delayed from the temperature peaks by one day, one was delayed by two days and two were delayed by three days.

The example of cross-correlation between N_2O and lagged-temperature for the period from June 15 to October 31, 2007 is shown on Figure 4.4a. A positive lag value indicates that the flux measurement followed the temperature measurement by that given lag in days. As one can see, N_2O flux is weakly, positively correlated with the temperature two to three days before the given measured flux. N_2O flux is then weakly, negatively correlated with the temperature approximately both a week before and after the measured flux. Obviously, there is no apparent physical mechanism that should make temperature after a given flux measurement have any causative effect on the measurement, but may simply reflect the fact that temperature is cyclical and a high temperature is eventually followed by a low temperature. Indeed, a plot of autocorrelation of temperature (Figure 4.4b) shows that temperature has a near zero correlation at positive and negative lags of about a week.

Our daily measurements showed largely cyclical nature of daily temperatures (Figure 4.1a), and N_2O flux did not necessarily follow the same cyclical path. Both frequently changing temperature cycles and delays in generated N_2O response likely contributed to the low correlation between temperature and N_2O fluxes. To eliminate the effect of frequent temperature changes, the daily rates of change were calculated for N_2O fluxes and temperatures by subtracting preceding daily values from subsequent ones. When a data gap of 1-2 days was observed, two closest values were subtracted and the difference divided by the number of days. When more than 2 days of data were missing, the rates of change for the next available day were omitted. The results for the N_2O peaks >0.05μg m^{-2} s^{-1} are shown in Figure 4.5, and N_2O flux and temperature were better correlated (R^2= 0.32, $P \leq$ 0.05) for their daily rates of change than their absolute values.

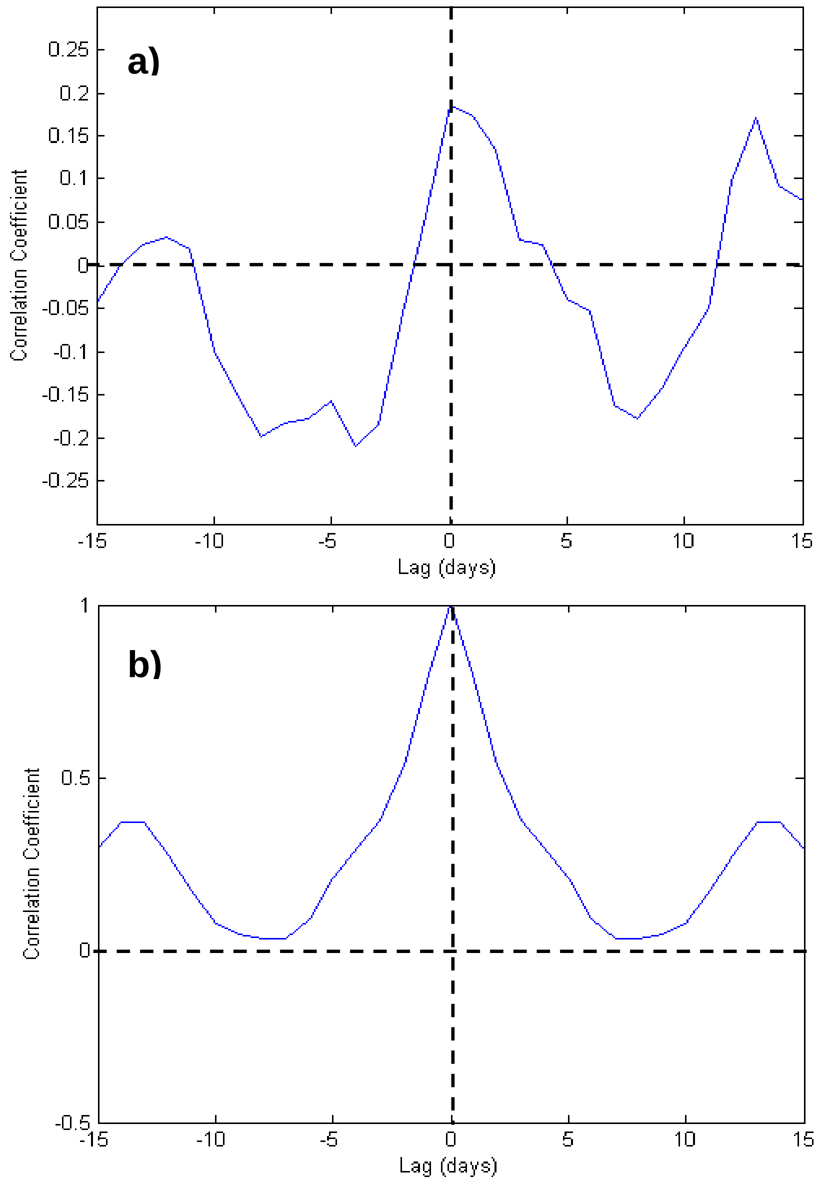

Figure 4.4. Cross-correlation between N_2O emissions and lagged-temperature (a) and autocorrelation of temperature (b) for the data measured from June 15 to October 31, 2007

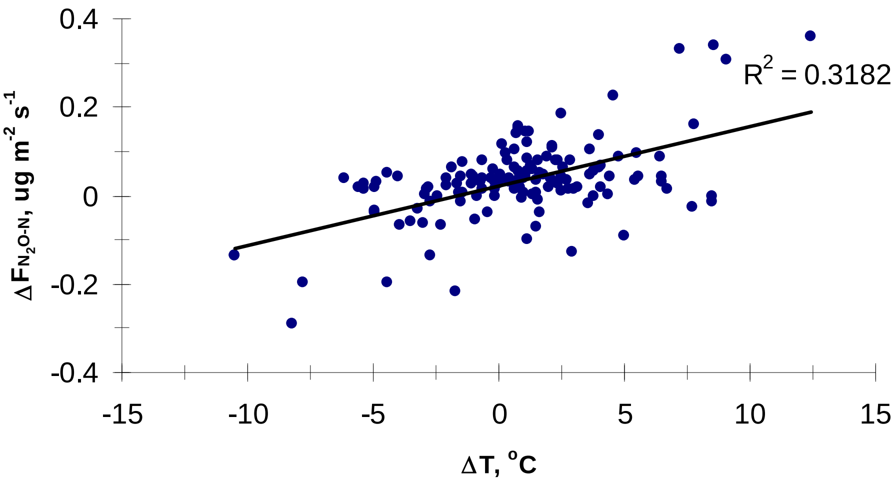

Figure 4.5.The correlation between rates of change for N_2O-N daily fluxes ($\Delta F = \frac{F_n - F_{(n-i)}}{i}$) and daily temperatures ($\Delta T = \frac{T_n - T_{(n-i)}}{i}$), where *F* is daily N_2O-N flux, µg m-2 s-1; *T* is daily air temperature, ^oC; *n* is the observation day; *i* is the time gap between days with available data.

4.4.3 Annual N_2O flux distribution

The observations clearly demonstrated a strong, event-driven nature of high N_2O peaks which mostly occurred either in summer following large rainfall events, or in early spring resulting from the spring thaw. Although the magnitude and intensity of N_2O peak fluxes were directly related to available N regulated by the amount and timing of manure spreading (Molodovskaya et al., 2009a), weather factors were the major emission triggers.

The N_2O flux distribution was different for the summer and winter emission events, when short abrupt summer fluxes followed the zero-high-zero pattern, whereas long-lasting winter N_2O emissions presented the continuous elevated baseline with a few spikes formed atop. Scanlon and Kiely (2003) reported similar seasonal trend in N_2O

high peak distribution and attributed it to the conceptual "hole-in-pipe" model by Firestone and Davidson (1989) for N_2O emissions and the effect of temperature acting as a "valve" regulating N_2O flow rate through the "hole". The N_2O loss to the atmosphere is therefore accelerated by the warmer temperature during the summer and slowed down by the colder temperature during the winter.

Although single N_2O events triggered by the intense summer precipitation can be very high and contribute a significant share of annual emissions, their occurrence is largely incidental and depends on the short-term weather conditions. The N_2O emissions from the spring thaw, a regular climatic pattern, showed more consistent year-to-year appearance. For instance, the cold winter in 2009 generated a spring thaw-induced N_2O event even in the absence of manure fertilization, although it had much smaller magnitude and shorter duration than in the previous years when manure N was abundant. Our study, therefore, confirmed the significance of spring thaw as a permanent seasonal trend for N_2O emissions in temperate regions that was previously discussed in the literature (Wagner-Riddle and Thurtelll, 1998; Maggiotto and Wagner-Riddle, 2001; Wagner-Riddle et al., 2007).

4.5 Conclusions

The long-term study of N_2O emissions from manure fertilized fields in New York State indicated that most of the annual N_2O flux was generated in form of event-induced high peaks which followed strong seasonal patterns. Whereas availability of manure N determined intensity and duration of N_2O peaks, abrupt weather changes (such as summer precipitation and early spring thaw events) that affected soil moisture and temperature status were the major N_2O event triggers. Soil moisture had a pronounced effect on N_2O emissions at extreme values (~90% WFPS), however, when it varied within narrow range of 50-65% WFPS, temperature was the stronger factor governing N_2O formation. Nevertheless, the relationship between N_2O flux and temperature was not straightforward due to delays in N_2O response to frequently changing temperature cycles. Combination of summer manure spreading and strong rainfall in June-July 2006 produced the most intense single N_2O peak event; however, spring thaw-induced N_2O fluxes were more consistent from year to year and were observed even in the absence of a recent fertilization. Our study confirmed previous findings about spring thaw as a permanent seasonal pattern for N_2O high peaks.

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CHAPTER 5

SUMMARY AND CONCLUSIONS

High temporal and spatial variability in N_2O flux distribution has been commonly reported in the literature. Microbial processes generating N_2O in soils are well documented; however due to the high sensitivity to the soil moisture and temperature changes, soil N_2O formation is highly dependent on random “hot spots” formed by the soil anisotropy, which makes extrapolation of process-level regularities to the larger scales difficult. In addition, the episodic nature of N_2O fluxes, which often follow environmental changes on the hours-to-days time scale, with peak values sometimes exceeding background by orders of magnitude, presents a serious challenge for measurement methodologies. To avoid possible errors in cumulative N_2O emission estimates, high-frequency flux observations on the continuous long-term basis are necessary. The micrometeorological eddy covariance method calculates flux as the mean product of instantaneous vertical wind speed and gas concentration in the air and provides high-precision, high-frequency, real-time N_2O emission data.

The eddy covariance monitoring of N_2O fluxes from agricultural manure-fertilized fields was conducted at New York State dairy farm in 2006 to 2009. The results demonstrated that manure nitrogen was the most important factor controlling the extent and magnitude of N_2O formation and release. The comparison between manure loads and cumulative emissions as well as the analysis of source contributions into the integrated flux showed that areas which received more manure N were stronger N_2O emitters. The absolute values of N_2O fluxes largely varied from year to year, however cumulative annual emissions estimated as a percentage of applied manure N were relatively close to the IPCC default. Supported by favorable environmental conditions, summer manure application resulted in the greatest N_2O emission factor (1.1% of applied manure N) although the greatest absolute flux values were observed from winter-fertilized fields.

Most of the N_2O flux was generated in form of event-induced high peaks that occurred within ~10% of observation time but contributed up to 50% of cumulative annual N_2O emissions. The analysis of the temporal distribution of fluxes showed that it followed strong seasonal patterns. N_2O peak events were primarily driven by strong rainfall and warm temperatures in growing season and soil thaw in winter and early spring. Those environmental changes affecting soil moisture and temperature status were the major N_2O event triggers, whereas availability of manure N determined a magnitude of N_2O fluxes. The most intense single N_2O peak event was produced from combination of summer manure spreading and strong rainfall in June-July 2006, however spring thaw-induced N_2O fluxes were more consistent from year to year and were observed even in the absence of a recent fertilization. Spring thaw was a permanent seasonal pattern for N_2O high peaks, as many of them were produced at the temperatures at or around freezing.

Both soil moisture and temperature conditions effected N_2O release. Changes in soil moisture had a pronounced effect on N_2O emissions at extreme values (65-90% WFPS), however, at lower values and within more narrow range (50-68% WFPS), it was poorly correlated with N_2O fluxes. Under these conditions, air and soil temperatures likely were stronger limiting factors. However, the relationship between N_2O flux and temperature was not straightforward due to delays in N_2O response to frequently changing temperature cycles.

The short-term static chamber campaign conducted in parallel with EC monitoring in summer 2008 showed the importance of using different scale techniques for N_2O source/sink studies. Both methods demonstrated similar N_2O daily estimates, although high variability of the fluxes largely contributed to uncertainty between the two data sets. The variability of chamber data was mainly caused by high spatial heterogeneity of soil N_2O formation, which resulted in both net N_2O production and consumption. Chamber measurements also showed significant negative N_2O fluxes indicating soil N_2O uptake which has to be taken into account while estimating N_2O budget. The EC fluxes were strongly dependent on wind direction and contributing footprint, so it is important to distinguish possible sources of emissions when the integrated flux is measured over non-uniform landscapes.

The N_2O emission data quality can be improved by using combined different scale N_2O measurements, such as conventional static chambers and footprint-integrated micrometeorological methods, for instance, during short-term field campaigns. The complementary use of the two methods may compensate for each other's shortcomings and thus help in reducing temporal and spatial variability of N_2O estimates.